On the Catalytic Action of Japanese Acid Earth. XI. The Isomerisation of Aldehydes to Ketones and the Explanation of the Migration of the Radicals from the Standpoint of the Electronic Theory (*Continued and concluded*).

By Koshiro ISHIMURA.

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α-o-*Tolyl α*-p-*tolyl ethylene glycol.* *p*-Methylbenzoyl carbinol (9.5 g) was added to the Grignard reagent (44 g. *o*-iodotoluene and 4.8 g. magnesium). After all of the carbinol was added the reaction mixture was boiled for 3 hours. It was cooled and treated with acetic acid (15 g. glacial acetic acid in 300 c.c. ice water). The upper ethereal solution was washed with dilute caustic soda, saturated solution of sodium chloride, and sodium bisulphite and again with brine. The ether was removed and the residue was subjected to the steam distillation for 5 hours. The contents of the flask were left to stand overnight. The main part (14.5 g.) of the required glycol settled down to the bottom forming yellowish solid mass, while a small portion (0.9 g.) of it was found to be suspending in water forming colourless needles, which crystallised from dilute alcohol in colourless needles, m.p. 115–116°C. (Found: C, 78.5; H, 7.7. $C_{16}H_{18}O_2$ requires C, 78.3; H, 7.4%).

The benzoyl derivative was obtained by Schotten-Baumann's method. It crystallised from 95% alcohol in colourless columns or needles, m.p. 164–165°C. (to a yellow melt). It has one molecule of water of crystallisation alike benzoyl *m*-toyl *p*-toyl ethylene glycol. (Found: C, 76.1; H, 6.0%; Mol. wt., (Rast), 325. $C_{23}H_{22}O_3 \cdot H_2O$ requires C, 75.8; H, 6.6%; Mol. wt., 364).

Oxidation of α-o-*tolyl α*-p-*tolyl ethylene glycol.* The glycol (0.83 g.) was added by portions to chromic oxide (1.2 g.) dissolved in 80% acetic acid (50 c.c.) and heated to boiling for a short time and left to stand overnight. It was neutralised with dilute caustic soda, extracted with ether, the ethereal extract washed with a solution of sodium chloride, dried over calcium chloride, the ether distilled off leaving an oil (0.55 g.), the crude *o*-tolyl *p*-tolyl ketone. The oxime produced from the ketone crystallised from dilute alcohol in colourless needless, m.p. 120°C. W. Scharwin and Schorygin[68] described the ketone as an oil boiling at 316–318°C./760 mm., characterised by an oxime melting at 122°C. The oxime was converted to *o*-toluyl *p*-toluidide through the Beckmann rearrangement, m.p. 144°C. (Found: N, 6.6. $C_{15}H_{15}ON$ requires N, 6.2%), which has also been given by the above-mentioned Russian authors.

o-*Tolyl* p-*tolyl actaldehyde.* A mixture of *α*-*o*-tolyl *α*-*p*-tolyl ethylene glycol (30 g.), crystalline oxalic acid (75 g.) and water (30 c.c.) was gently boiled for 3 hours, carbon dioxide being meanwhile passed into

(68) *Ber.*, **36** (1903), 2025.

the reaction vessel in order to prevent the oxidation of the product with atmospheric oxygen. The upper layer of the contents of the vessel was extracted with ether, the ethereal extract washed with dilute caustic soda and with water, dried over anhydrous sodium sulphate and the ether was removed by distillation. The residue was distilled in the reduced pressure of 9 mm. giving the fractions shown in Table 2.

Table 2.

Fractions	B.p. (°C.)	Yield (g.)
(1)	140–165	1.1
(2)	165–175	3.0
(3)	175–180	3.0
(4)	180–182	5.4
(5)	182–205	3.5
(6)	Residue	—

The fraction (1) consists chiefly of *p*-methylbenzoyl carbinol still remaining. The fraction (4). is the required aldehyde, d_4^{20}, 1.0669; n_D^{20}, 1.5812; M.R., found, 69.96; calc. (Eisenlohr), 68.90. (Found: C, 85.4; H, 7.5. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%).

The aldehyde unites with sodium bisulphite very difficultly obviously owing to the steric hindrance of the methyl group attached to the carbon atom next to the carbonyl. A small quantity of *o*-tolyl *p*-tolyl ketone, which is still more difficult than the foregoing ketone to produce the addition compound with bisulphite, was found to be produced thereby. Its existence was confirmed by the production of *o*-toluyl *p*-toluidide, m.p. 143–144°C., (Found: N, 6.5. $C_{15}H_{15}ON$ requires N, 6.2%), from the oxime through the Beckmann rearrangement. The melting point did not depress by mixing it with the condensation product of *o*-toluic acid and *p*-toluidine.

o-Tolyl *p*-tolyl acetaldehyde forms a faintly yellow, viscous oil, and turns blue when brought to contact with Fuchsin-bisulphite solution. The semicarbazone crystallised from dilute alcohol in thick prisms, m.p. 154–155°C. (to a yellow melt). (Found: N, 15.2. $C_{17}H_{19}ON_3$ requires N, 14.9%).

o-*Tolyl* p-*tolyl acetic acid.* Potassium hydroxide (5 g. dissolved in 50 c.c. water) was added by portions (5 c.c. at a time every ten minutes) to the mixture of *o*-tolyl *p*-tolyl acetaldehyde (3 g. dissolved in 60 c.c. alcohol) and silver nitrate (7 g. dissolved in 7 c.c. water), and the mixture was shaken vigorously meanwhile. It was filtered, the filtrate saturated with carbon dioxide, concentrated on the water bath. The remaining aldehyde was thereby thrown down as oil drops, which were separated on filter paper. The filtrate was neutralised with dilute sulphuric acid. An oily substance separated, and solidified on cooling and crystallised from hot water in glittering plates (0.8 g.), m.p. 115–116°C. (Found: C, 80.2; H, 7.0%; Equiv. wt. (by titration with 1/20 N alkali solution), 239.8. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%; Equiv. wt., 240.1).

o-*Tolyl* p-*methylbenzyl ketone.* Attempts to prepare the above ketone by the condensation of *ω*-brom-*o*-methylacetophenone with toluene in the presence of anhydrous aluminium chloride failed, while the oxidation of *o*-tolyl *p*-methylbenzyl carbinol resulted in the formation of the impure ketone difficult to be purified. The pure ketone was obtained only by the isomerization of *o*-tolyl *p*-tolyl acetaldehyde. It melts at 26°C.

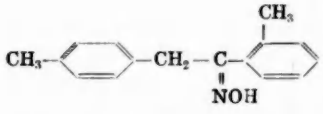
The preparation of the ketone from *o*-tolyl *p*-methylbenzyl carbinol was carried out in the following way. *p*-Tolyl acetaldehyde (2 g. dissolved in 2 c.c. ether) was added to the Grignard reagent (3.26 g. of *o*-tolyl iodide and 0.36 g. of magnesium), the reaction mixture was boiled for 2 hours and left to stand overnight. A small quantity of ice water was added to the product, followed by 36% hydrochloric acid (1.2 c.c.). It was then treated as usual and a yellow thick oil (1.3 g.) was obtained, which showed no tendency to solidify when cooled. The raw *o*-tolyl *p*-methylbenzyl carbinol (0.80 g.) thus obtained was dissolved in 80% acetic acid (30 c.c.) and chromic oxide (0.15 g.) was added to the solution little by little. The solution was boiled for 30 minutes, cooled and poured into ice water (400 c.c.), the water solution extracted with ether, the ethereal extract was washed with aqueous sodium hydroxide and with a solution of sodium chloride, dried over calcium chloride and the ether removed. A semi-solid yellow mass (0.37 g.) with aromatic odour was obtained, which did not solidify when cooled at −15°C. for 12 hours. Attempts to obtain the oxime from the ketone considered to have thus been produced resulted in the formation of viscous oil which again did not solidify when cooled at −5°C. It was dissolved in ether and treated with phosphorus pentachloride and the well defined crystals of [*p*-tolyl acetyl]-*o*-toluidide (0.05 g.), m.p. 163°C. (uncorr.), was finally obtained showing that the required ketone has actually been synthesised. The melting point was not depressed by mixing it with the authentic specimen mentioned below.

As mentioned above and will be described below in detail *o*-tolyl *p*-methylbenzyl ketone was produced by the isomerization of *o*-tolyl *p*-tolyl acetaldehyde and melted at 26°C. when recrystallised from dilute alcohol. (Found: C, 85.8; H, 7.1. $C_{16}H_{16}O$ requires C, 85.7; H. 7.1%). It is slowly oxidised with atmospheric oxygen to *o*- and *p*- toluic acids.

The oxime (0.19 g.) was obtained from the ketone (0.3 g.) by Auers' method, which melted at 96–103°C. after recrystallisation three times from dilute alcohol. It was subjected to the fractional crystallisation and gave the following fractions:—

Fractions	M.p. (°C.)	Yields (in g.)
(1)	109–115	0.06
(2)	77– 84	0.05
(3)	75– 80	0.02

The first fraction (m.p. 109–115°C.) gave [*p*-tolyl acetyl]-*o*-toluidide by the Beckmann rearrangement indicating the configuration of the oxime as follows:—



[*p*-Tolyl acetyl]-*o*-toluidide was also obtained by the condensation of *p*-tolyl acetic acid and *o*-toluidide in flat needles, m.p. 165°C. (corr.) (Found: N, 5.8. $C_{10}H_{17}ON$ requires N, 5.9%), and the isomeric compound

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o-toluyl *p*-methylbenzylamine by the condensation of *o*-toluic acid and *p*-methylbenzylamine in leaflets, m.p. 114°C. (Found: N, 6.1. $C_{16}H_{17}ON$ requires N, 5.9%).

The semicarbazone of *o*-tolyl *p*-methylbenzyl ketone was obtained in the usual way. It crystallised from dilute alcohol in colourless needles, m.p. 172°C. (corr.) (decomp.).

p-*Tolyl* o-*methylbenzyl ketone.* The ketone (7.5 g.) was obtained by the condensation of *o*-tolyl acetyl chloride (6.5 g.) with toluene (30 c.c.) in the presence of anhydrous aluminium chloride (6 g.) It was recrystallised from dilute alcohol forming colourless scales, 86–87°C. (Found: C, 85.4; H, 7.5. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%).

o-Tolyl acetyl chloride, obtained from the corresponding acid and thionyl chloride, boiled at 175°C under 28 mm. with slight decomposition. According to P. Hill and W. F. Short[69] it boils at 106–107°C. under 10 mm· and A. E. Bradfield, B. H. Hedge, B. S. Rao, J. L. Simonsen and A. E. Gillam gave the boiling point 111–112°C. under 16 mm.

The semicarbazone crystallised in bundled needles on the 54th day of standing of the solution of the ketone (0.9 g.), semicarbazide hydrochloride (0.9 g.) and potassium acetate (0.9 g.) in dilute alcohol (10 c.c. of 95% alcohol mixed with 4 c.c. of water). It was recrystallised from dilute alcohol in colourless needles, m.p. 185–186°C. (corr.) (decomp.) (Found: N, 6.3. $C_{16}H_{17}ON$ requires N, 5.9%).

Isomerization of o-*tolyl* p-*tolyl acetaldehyde.* The aldehyde (15.0 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C. at a rate of 3.3 g. per hour being accompanied by the slow flow of carbon dioxide. A heavy yellowish oil (a) mixed with drops of water (8.8 g. in total) was collected in the receiver in the course of the passing and during the lapse of 1 hour after the passing of all of the aldehyde into the reaction tube. The tube was then evacuated at 300°C. and 0.9 g. of a yellow oil (b) were obtained. When the temperature was raised to 350°C. under the reduced pressure, 0.1 g. of a reddish viscous oil (c) came out. All (a), (b) and (c) showed no colour reaction characteristic to aldehydes.

The product (a) was freed from the water drops with anhydrous sodium sulphate and distilled, giving a fraction (0.9 g.) which boiled at 100–115°C. obviously consisting of mainly toluene. The residue (7.3 g.) was distilled under the reduced pressure of 4 mm. giving the fractions shown in Table 3.

Table 3.

Fractions	B.p. (°C.)	Yields (g.)	Remarks
(1)	145–165	1.3	Yellow oil with aromatic odour.
(2)	165–172	0.9	,,
(3)	172–180	3.6	Yellow viscous oil, odourless.
(4)	Residue	1.5	,,

(69) *J. Chem. Soc.*, **1935**, 1125.
(70) *Ibid.*, **1936**, 675.

The fractions (1) and (2) in Table 3 manifested no apparent change when cooled at –15°C. for 21 hours. The fraction (3) was converted to a mush when similarly treated, which melted on touching with the hand. It was recrystallised from dilute alcohol in colourless columns, m.p. 26°C., and confirmed to be *o*-tolyl *p*-methylbenzyl ketone through the Beckmann rearrangement of its oxime as described above.

The fraction (4) was changed to a mush by standing at the ordinary temperature for several days and a small amount of *p*-tolyl *o*-methylbenzyl ketone, m.p. 86–89°C., was obtained from it, which was identified by the mixed melting point with the sample synthesised as stated above.

The ratio of the amount of *o*-tolyl *p*-metylbenzyl ketone to that of *p*-tolyl *o*-methylbenzyl ketone, both produced by the isomerisation of *o*-tolyl *p*-tolyl acetaldehyde, was estimated about 4:1.

p-*Chlorobenzoyl methyl acetate.* Potassium acetate (200 g.) dissolved in alcohol (300 c.c.) was added to *p*-chlor-*ω*-bromacetophenone (170 g.) dissolved in hot alcohol (500 c.c.) and the mixture was heated for a while and left to stand. On the next day a large amount of potassium bromide was found thrown down, which was filtered and the filtrate concentrated on the water bath and left to cool down to the ordinary temperature. *p*-Chlorobenzoyl methyl acetate (102 g.) separated forming glittering scales, m.p. 71.5–72.5°C., when recrystallised from ligroin (b.p. 80–120°C.). (Found: Cl, 16.8. $C_{10}H_9O_3Cl$ requires Cl, 16.7%).

p-*Chlorobenzoyl carbinol.* Barium carbonate (50 g.) was added to the boiling water (200 c.c.) followed by *p*-chlorobenzoyl methyl acetate (40 g.) and the mixture was boiled for 1 hour. It was filtered hot and the insoluble matter remaining on the filter paper was extracted with hot water, the extract combined with the filtrate. On cooling the combined liquid, *p*-chlorobenzoyl carbinol (28 g.) separated. It was recrystallised from ligroin in colourless needles, m.p. 123–126°C. (uncorr.) (decomp.) (Found: Cl, 20.7. $C_8H_7O_2Cl$ requires Cl, 20.8%).

α-p-*Chlorophenyl α*-p-*tolyl ethylene glycol.* *p*-Chlorobenzoyl carbinol (11 g.) was added little by little in the form of crystalline powder to the Grignard reagent prepared from *p*-iodotoluene (50 g.) and magnesium. A vigorous reaction occurred. The reaction mixture was boiled for 2 hours and left to stand overnight. It was treated with cold dilute acetic acid (12 g. of glacial acetic acid in 200 c.c. of ice water). The upper ethereal solution was washed with dilute caustic soda and then with water and the ether was removed. The residue solidified on cooling. It was subjected to the steam distillation, toluene and other volatile impurities being thereby removed. The required glycol remained in the distilling flask, which on cooling solidified to a yellowish mass. It was recrystallised from ligroin in colourless needles (17 g.), m.p. 132–133°C. (uncorr.) (Found: Cl, 13.4. $C_{15}H_{15}O_2Cl$ requires Cl, 13.5%).

The benzoyl derivative obtained by the usual method crystallised from dilute alcohol in fine needles, m.p. 145–146°C. Mol. wt. (Rast), 358.2. $C_{22}H_{19}O_3Cl$ requires 366.5.

p-*Chlorophenyl* p-*tolyl acetaldehyde.* A mixture of *α*-*p*-chlorophenyl *α*-*p*-tolyl ethylene glycol (40 g.), crystalline oxalic acid (100 g.) and water (40 c.c.) was heated in an oil bath for 3 hours, the slow flow of carbon dioxide being passed into the mixture meanwhile. The tempera-

ture was maintained at 115°C. while that of the oil bath showed 140°C. After cooling the content of the vessel was extracted with ether, the ethereal solution washed with dilute caustic alkali, saturated solution of sodium chloride and with water, dried over calcium chloride. The residual oil (38 g.) obtained by removal of the ether was distilled under the reduced pressure of 6 mm. giving the results shown in Table 4.

Table 4.

Fractions	B.p. (°C.)	Yields (g.)
(1)	150–197	2.2
(2)	197–200	20.9
(3)	Residue	11.0

The fraction (2) was purified through the addition compound of sodium bisulphite and pure *p*-chlorophenyl *p*-tolyl acetaldehyde was obtained as a faintly yellow oil, b.p. 195–197°C./5 mm.; d_4^{22}, 1.1805; n_D^{22}, 1.5896 M.R., found, 69.85, calc. (Eisenlohr), 69.15. (Found; Cl. 14.4. $C_{15}H_{13}OCl$ requires Cl, 14.5%). It tinges fuchsin-sulphurous-acid solution with blue colour. It is oxidized slowly in the presence of air and light at the ordinary temperature to produce *p*-chlorophenyl acetic acid. The semicarbazone prepared in the usual way dissolved difficultly in dilute alcohol; it was recrystallised from a mixture of toluene and ligroin (1:1) in white powder, m.p. 159–160°C. (uncorr.) (to a yellow melt). (Found: N, 14.1. $C_{16}H_{16}ON_3Cl$ requires N, 13.9%).

p-*Chlorophenyl* p-*tolyl acetic acid.* The acid (1.3 g.) was obtained from *p*-chlorophenyl *p*-tolyl acetaldehyde (4.0 g.) by the method similar to that employed for the oxidation of *o*-tolyl *p*-tolyl acetaldehyde. It was recrystallised from ligroin in clustered needles in stellar form, m.p. 145.5°C. (uncorr.). (Found: Cl, 13.4; Mol. wt. (by titration with 1/20 N sodium hydroxide), 261.5. $C_{15}H_{13}O_2Cl$ requires Cl, 13.6%; Mol. wt., 260.5).

p-*Chlorophenyl* p-*tolyl ketone.* (a) *α-p*-Chlorophenyl *α-p*-tolyl ethylene glycol (0.30 g.) was dissolved in 80% acetic acid (20 c.c.) and chromic oxide (0.32 g. dissolved in a small quantity of water) was added to the solution and the mixture was left to stand overnight. It was heated on the water bath for 20 minutes and cooled. Glittering scales (0.25 g.) crystallised out, of which the amount increased on the addition of water. It was separated by filtration, washed with water and recrystallised from dilute alcohol in colourless scales, m.p. 128–129°C. (uncorr.) (Found: Cl, 15.3. $C_{14}H_{11}OCl$ requires Cl, 15.4%).

(b) *p*-Tolyl acetyl chloride (4.0 g.) was condensed with chlorobenzene in the presence of anhydrous aluminium chloride and the required ketone (0.36 g.) thus obtained was recrystallised from dilute alcohol in faintly reddish scales.

(c) When *p*-chlorophenyl *p*-tolyl acetaldehyde was purified through the addition compound of sodium bisulphite a small amount of a substance very difficult to react with the bisulphite was obtained which was confirmed to be *p*-chlorophenyl *p*-tolyl ketone.

(d) On long standing *p*-chlorophenyl *p*-tolyl acetaldehyde was partly changed to *p*-chlorophenyl *p*-tolyl ketone.

All the four specimens described above showed the same melting point which was not depressed when mixed with one another. W. D.

Cohen[71] obtained the same ketone by the condensation of *p*-chlorobenzoyl chloride and toluene and gave the melting point 118°C. (very probably a typographical error for 128°C.).

p-*Tolyl* p-*chlorobenzyl ketone.* Phenyl acetic acid (22 g.) was nitrated following the information given by W. Borsche[72] resulting in *p*-nitrophenyl acetic acid (15 g.) which on reduction by the method described in "Organic Syntheses"[73] gave *p*-aminophenyl acetic acid (10·4 g.). The amino acid was changed to *p*-chlorophenyl acetic acid (4.0 g.) and then to *p*-chlorophenyl acetyl chloride (4.0 g.) which was condensed with toluene (20 c.c.) in the presence of anhydrous aluminium chloride (6 g.). The reaction mixture was treated with ice water and the crystals thereby separating (6.0 g.) were recrystallised from dilute alcohol in colourless glittering plates, m.p. 113.5°C. (uncorr.). (Found: Cl, 14.4. $C_{15}H_{13}OCl$ requires Cl, 14.5%). L. Szëgo and P. Ostinelli[74] gave the melting point 113°C. Attempts to obtain the ketone from *p*-methyl *ω*-bromacetophenone and chlorobenzene resulted in no good result.

The semicarbazone prepared in the usual way formed colourless needles m.p. 191–192°C. (uncorr.) (decomp.). (Found: N, 5.5. $C_{15}H_{14}ONCl$ requires N, 5.4%). The oxime was prepared in the usual way. It was recrystallised from dilute alcohol in glittering plates, m.p. 136–137°C (uncorr·). (Found: N, 5.5. $C_{15}H_{14}ONCl$ requires N, 5.4%).

p-*Chlorophenyl* p-*methylbenzyl ketone.* The raw *p*-tolyl acetyl chloride prepared from *p*-tolyl acetic acid (4 g.) and thionyl chloride (12 g.) was added drop by drop to chlorobenzene (20 c.c.) mixed with anhydrous aluminium chloride (6 g.), the mixture being cooled with ice water meanwhile. After 4 hours' standing, it was treated with ice water, washed with dilute alkali and then with water, dried over calcium chloride and the excess chlorobenzen was removed leaving resinous brown mass (4 g.), which was recrystallised from dilute alcohol in colourless scales (1.2 g.), m.p. 103.5°C. (Found: Cl, 14.6 $C_{15}H_{13}OCl$ requires Cl, 14.5%). L. Szëgo and P. Ostinelli[75] gave the melting point 123°C.

The semicarbazone crystallised from dilute alcohol in colourless needles, m.p. 151–152°C. (Found: N, 13.9. $C_{16}H_{16}ON_3Cl$ requires N, 13.9%). The oxime crystallised from dilute alcohol in colourless needles, m.p. 106–107°C. (Found: N, 5.7. $C_{15}H_{14}ONCl$ requires N, 5.4%).

Isomerization of p-*chlorophenyl* p-*tolyl acetaldehyde.* The aldehyde (18.0 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C at a rate of 4.5 g. per hour, being accompanied by the slow current of carbon dioxide. A yellow oil (a) mixed with a small amount of crystals (1.6 g. in total) was first collected and then a viscous yellow oil (b) (4.5 g.) came out which soon solidified on cooling. By evacuating the reaction tube at the same temperature a blackish oil (c) (4.5 g.) was obtained which likewise solidified at once. The product (b) was separated into two parts by fractional crystallisation from ligroin, i.e., (i) (3.0 g.) less soluble in the solvent and (ii) (1.5 g.) more soluble in it. The product

(71) *Rec. Trav. Chim. Pays-Bas.*, **38** (1919), 117.
(72) *Ber.*, **42** (1909), 3596.
(73) Coll. Vol. I, (1932), 44.
(74) *Gazz. chim. ital.*, **60** (1930), 677; *Chem., Abst.*, **25** (1931), 1524.
(75) *Loc. cit.*

(i) was recrystallised once more from ligroin forming colourless scales (2.7 g.) melting at 104–105.5°, from which the following fractions were obtained by fractional crystallisation three times from ligroin:—

Table 5.

Fractions	Yields (g.)	M.p. (°C.)	Thawing point (°C.)	Remarks
(1)	2.31	105.6	103	Colourless scales.
(2)	0.20	104	101	,, ,,
(3)	0.15	95–98	—	Yellowish scales.
(4)	0.02	170–195	—	Colourless powder.

The fraction (1) in Table 5 may safely be stated to consist of *p*-chlorophenyl *p*-methylbenzyl ketone (ca. 80%) and *p*-tolyl *p*-chlorobenzyl ketone (ca. 20%) by referring it to Fig. 1. (p. 201). The fraction (1) melted at 103.5–104°C. when mixed with the former ketone (m.p. 103.5°C.) and at 108°C. with the latter (m.p. 113.5°C.). The fraction (2) is richer in *p*-chlorophenyl *p*-methylbenzyl ketone than the fraction (1). The fraction (3) is obviously very impure, and the fraction (4) was not further studied of which the melting point was found much higher than those of both the above ketones.

The product (ii) mainly consisted of oily substance mixed with a small quantity of solid matter which was recrystallised several times from dilute alcohol forming colourless glittering scales (0.15 g), m.p. 101°C.; thawing point, ca. 85°C, probably *p*-chlorophenyl *p*-methylbenzyl ketone mixed with a small quantity of impurities.

The product (c) was treated similarly to (b); it was first separated into two parts, i.e., (i) (3·0 g.) less soluble in ligroin, m.p. 100–104°C. and (ii) (1.5 g.) more soluble in it. The part (i) was once more recrystallised from ligroin forming light yellow scales which melted at 106.5–107.5°C. alone, and at 105–106°C. when mixed with pure *p*-chlorophenyl *p*-methylbenzyl ketone (m.p. 103.5°C.), revealing the composition of 59% of this ketone and 41% of *p*-tolyl *p*-chlorobenzyl ketone. It was recrystallised several times from dilute alcohol giving the following fractions:—

Table 6.

Fractions	Yields (g.)	M.p. (°C.)	Thawing point (°C.)	Remarks
(1)	0.02	107.5	106.7	—
(2)	1.34	108.0	107.1	Yellowish scales.
(3)	0.31	107.0	106.0	Colorless scales.
(4)	6.27	104.3	102.0	Yellow scales.
(5)	0.09	95–99.5	—	—

0.4 g. of the fraction (2) in Table 6 gave the oxime (0.3 g.) which was fractionated over ten times affording colourless needles (0.09 g.), m.p. 106–107°C. alone or mixed with *p*-chlorophenyl *p*-methylbenzyl ketoxime, and a small quantity of needles which melted alone at 122–126°C., and at 128–134°C. when mixed with *p*-tolyl *p*-chlorobenzyl ketoxime (m.p. 136–137°C.). By the repeated fractional crystallisation of the semicarbazone obtained from the fraction (2) in Table 6, a small quantity of a fraction was obtained which melted at 187–189°C. alone, and at 188–189°C. when mixed with the semicarbazone of *p*-tolyl *p*-chlorobenzyl ketone (m.p. 191–192°C.).

More soluble part of the product (c), (p. 300) was recrystallised several times from dilute alcohol and gave 0.62 g. of yellowish scales melting at about 96°C. and 0.04 g. of yellowish scales melting at about 95°C. Both may very probably be impure *p*-chlorophenyl *p*-methylbenzyl ketone.

Summary.

(1) All the phenomena hitherto ascribed to the characteristic catalytic action of Japanese acid earth can be explained by taking its strong electron-seeking property into consideration. Thus its ability to promote the hydrolysis of cane sugar or starch and the oxidation of pyrogallol and its property to give various oxidase-like colour reactions are all due to its selective adsorptive power for hydroxyl ion. The facts can similarly be explained that the dehydration or deamination of various organic compounds takes place through its catalytic action followed by the intramolecular rearrangement, as observed in the reaction of producing cyclopentane derivatives from cyclohexanol, cyclohexylamine or their methyl derivatives.

The initial step of the formation of β,β'-dinaphthyl from naphthalene in the presence of the earth is the polarisation of the naphthalene molecule promoted by its electron-seeking property.

(2) Several diarylacetaldehydes have been newly synthesised and found to rearrange themselves to give the corresponding ketones, when heated at 300°C. in the presence of the earth. Thus phenyl *p*-tolyl and *m*-tolyl *p*-tolyl acetaldehydes gave phenyl *p*-methylbenzyl and *m*-tolyl *p*-methylbenzyl ketones respectively, while *o*-tolyl *p*-tolyl and *p*-tolyl *p*-chlorophenyl acetaldehydes gave the respective mixtures of *o*-toly *p*-methylbenzyl and *p*-tolyl *o*-methylbenzyl ketones and of *p*-chlorophenyl *p*-methylbenzyl and *p*-tolyl *p*-chlorobenzyl ketones.

(3) By comparing the yields in the isomeric ketones thus produced the order of the facility of separation of the different aryl groups was determined as follows:—

Phenyl, *m*-tolyl>*p*-chlorophenyl>*o*-tolyl>*p*-tolyl.

The phenyl group may most probably have the greater migratory tendency than the *m*-tolyl.

(4) The mechanism of the conversion of the aldehydes to the ketones has been discussed. It has been postulated that an electromeric displacement of electrons in the carbonyl group $\overset{\frown}{C=O}$ is promoted by the

action of the earth, and one of the aryl groups migrates with its valency electrons from the adjacent α-carbon atom to the depleted carbonyl carbon. A proton is then splitted from the carbonyl carbon and unites with the carbonyl oxygen to give the enolic form of the ketone, isomeric to the aldehyde. The conclusion has been reached that the more electron-attracting of the two aryl groups must be first separated as anion.

(5) It was confirmed that the capacity of the *p*-tolyl group for electron-release is much larger than those of *o*-tolyl, *m*-tolyl, phenyl and *p*-chlorophenyl groups. By these results a new chemical evidence has been given for the tautomeric effect of the methyl group.

(6) Following compounds have been newly synthesised and their constitutions were confirmed:— α-phenyl α-*p*-tolyl, α-*m*-tolyl α-*p*-tolyl, α-*o*-tolyl α-*p*-*tolyl* and α-*p*-chlorophenyl α-*p*-tolyl ethylene glycols and their benzoyl derivatives; *p*-tolyl *m*-methylbenzyl, *m*-tolyl *p*-methylbenzyl, *o*-tolyl *p*-methylbenzyl, *p*-tolyl *o*-methylbenzyl, *p*-chlorophenyl *p*-methylbenzyl and *p*-tolyl *p*-chlorobenzyl ketones and their oximes and semicarbazones; *m*-tolyl *p*-tolyl, *o*-tolyl *p*-tolyl and *p*-tolyl *p*-chlorophenyl acetic acids; *p*-methylbenzoyl carbinol, *p*-chlorobenzoyl methyl acetate and *p*-chlorobenzoyl carbinol.

(7) *o*-Tolyl *p*-methylbenzyl and *m*-tolyl *p*-methylbenzyl ketones have been found to be oxidised slowly by the action of atmospheric oxygen on long standing, giving the mixtures of *o*-toluic and *p*-toluic acids and of *m*-toluic and *p*-toluic acids respectively, while the isomeric ketones, *p*-tolyl *o*-methylbenzyl and *p*-tolyl *m*-methylbenzyl ketones remained unchanged.

(8) The stereo-isomers of the oximes of the following ketones were isolated and their configurations were determined by carrying out the Beckmann rearrangement:— *m*-tolyl *p*-tolyl, *m*-tolyl *p*-methylbenzyl and *o*-tolyl *p*-methylbenzyl ketones.

For the identification of the products of the rearrangement the following compounds were newly synthesised:— *p*-toluyl *m*-toluidide, *m*-toluyl *p*-toluidide, [*p*-tolyl acetyl]-*m*-toluidide, *m*-toluyl *p*-methylbenzylamine, [*p*-tolyl acetyl]-*o*-toluidide and *o*-toluyl *p*-methylbenzylamine.

(9) α, β-Dibenzoyl ethane was confirmed to occur in the reaction product when ω-bromacetophenone was condensed with toluene by the Friedel and Crafts' reaction. The anticipated phenyl *p*-methylbenzyl ketone has not been isolated from the reaction product.

(10) It was found that the considerable quantity of *m*-tolyl *p*-tolyl ketone was produced when *m*-tolyl *p*-tolyl acetaldehyde is purified through its bisulphite compound or oxidised with moist silver oxide.

Similar facts have been observed in the cases of *o*-tolyl *p*-tolyl and *p*-chlorophenyl *p*-tolyl ketones. They were produced in the course of the purification of *o*-tolyl *p*-tolyl and *p*-chlorophenyl *p*-tolyl acetaldehydes respectively through the addition compounds of sodium bisulphite and by the autoxidation of the above-mentioned aldehydes on long standing in the presence of light and air.

(11) The semicarbazones of several above-mentioned ketones have been found very difficult to be produced. Thus the semicarbazone of *m*-tolyl *p*-tolyl ketone was formed after 22 days' standing of the dilute alcoholic solution of the ketone mixed with semicarbazide hydrochloride and potassium hydroxide and that of *p*-tolyl *o*-methylbenzyl ketone only

after 54 days. The semicarbazone of *m*-tolyl *p*-methylbenzyl ketone was not confirmed to produce even after 140 days' standing of the reaction mixture.

(12) Equilibrium diagrams of the systems of phenyl *p*-methylbenzyl and *p*-tolyl benzyl ketones and of *p*-chlorophenyl *p*-methylbenzyl and *p*-tolyl *p*-chlorobenzyl ketones have been drawn by applying the modified Rheinboldt's method. It was found that an eutectic point exists in the former system while a solid solution is formed in the latter. (*Concluded*).

The author wishes to express his gratitude to Dr. H. Inoue for his unfailing interest and encouragement.

The Tokyo Imperial Industrial Research Laboratory, Hatagaya, Tokyo.

Studien über Oxydationszersetzung des Methans (*Fortsetzung*).

Von Toyoziro OGURA.

(Eingegangen am 6. Juni 1941.)

III. Methan-Wasserdampf-Reaktionen.

Die Methan-Wasserdampf-Reaktion ist die wesentliche Reaktion des Oxydationszersetzung des Methans und hat zwei Reaktionsformen.

$$1 \qquad CH_4+H_2O = CO+3H_2$$

$$2 \qquad CH_4+2H_2O = CO_2+4H_2$$

Diese Reaktionen sind endothermisch. Die erste Reaktion tritt unter höherer Temperatur, die Zweite unter niederer Temperatur ein. Unter den vielen Verfahren, aus Methan Wasserstoff zu gewinnen sind diese Reaktionen die ergebigsten, d.h. sie geben die grösste Menge Wasserstoff aus einem Volum Methan.

Zur Zersetzung des Methans wurde bei den Untersuchungen die Wärmeenergie benutzt, man kann aber auch mit Elektrizität, Hochspannung im Vakuum, arbeiten.

Da der Katalysator bei der Oxydationszersetzung eine wichtige Rolle spielt, habe ich die katalytischen Eigenschaften einiger Materien studiert. Die erhaltenen Resultate passen gleichfalls auf andere Oxydationszersetzungen, wie Methan-Sauerstoff- oder Kohlendioxyd-Reaktionen.

Andere physikalischen und chemischen Eigenschaften des Katalysators, wie die Oberflächenbeschaffenheit, Aktivierung, Krystallstruktur usw. sowie der Reaktionsmechanismus, kommen hier nicht in Frage.

a) *Verfolgung der Katalysatoren.* Bei den Methan-Wasserdampf-Reaktionen spielt der Katalysator, wie oben erwähnt, eine wichtige Rolle. Man kann behaupten, dass die Qualität des Katalysators das wichtigste ist, was die Reaktionen beherrscht. Tafel 6 zeigt die Komponenten der Reaktionsgase ohne Katalysator. Bei 1000°C. ist der Zersetzungsgrad nur 16.2 und bei 1200°C. bleiben noch 12% des Methans unverändert.

Zersetzungsgrad wird nach der Formel $100(CO_2 + CO)/CO_2 + CO + CH_4$.

Aber bei Anwendung passender Katalysatoren erfolgt die Zersetzung schon besser, woraus die Wichtigkeit des Katalysators klar wird, wie in Tafel 7 erwähnt. Ich habe die Katalysatoren, die Nickel-Alumina-Kaolin Reihe, erst bei 500°C. kalziniert, bei 300°C. reduziert und dann gebraucht. $H_2O/CH_4=2.0$ bedeutet, dass das molare Verhältnis des Wasserdampfs und des Methans 2:1 ist.

Tafel 6.

Exp. Nr. b 105, ohne Kat. $H_2O/CH_4 = 2.5$, Gas. Ges. 5 lt/St.

Reakt. Temp. °C.	CO_2	C_nH_m	CO	H_2	CH_4	Z.G.
800	1.6	3.4	1.4	10.0	83.6	3.5
900	1.8	2.0	5.8	23.2	67.2	10.1
1000	2.0	1.4	8.7	32.2	55.7	16.1
1100	3.0	1.6	10.4	52.0[1]	33.0	28.4
1200	5.0	1.0	11.6	69.6[2]	12.8	56.5

Z.G. = Zersetzungsgrad des Methans

od. Z. G. a. $\dfrac{CO_2+CO}{CO_2+CO+CH_4}\times 100$

1) theo. Wert 43.2 2) theo. Wert 54.8

Tafel 7.

Exp. Nr. b 102.103, Kat. Nr. B 47., $H_2O/CH_4 = 2.5$, Gas. Ges. 5 lt/St.

Reakt. Temp. °C.	CO_2	CO	H_2	CH_4	Z.G. a
500	6.2	3.8	37.1	52.9	15.9
600	8.2	10.7	65.0	16.1	54.0
700	5.3	17.2	71.8	5.7	79.8
800	4.0	19.5	74.5	2.0	92.2
900	3.6	20.1	74.8	1.5	94.0
1000	2.2	22.7	74.3	0.8	96.8

Die Differenz zwischen den beiden oben beschriebenen Reaktionen besteht nicht nur im Zersetzungsgrad, sondern auch in der Art der Reaktionen. Ohne Katalysatoren bilden sich ungesättigter Kohlenwasserstoff und wenn die Erhitzung 1000°C. übersteigt so bildet sich eine Menge freien Kohlenstoffs (Russ). Das zeigt die Thermozersetzung des Methans nach der Gleichung $CH_4=C+2\,H_2$. Aus der Tafel 8 ersieht man, dass das Wasserstoffprozent im Reaktionsgase bei 1100°C. und 1200°C. resp. 52.0 und 69.6 sind, trotz der theoretischen Werte, die nach der Formel $4\,CO_2+3\,CO$ resp. 43.2 und 54.8% sein sollen. Bei höherer Temperatur über 1000°C. ist die Thermozersetzung bedeutender, als die Wasserdampfzersetzung des Methans, wie Gleichgewichtskonstanten zeigen. Die Verwendung passender Gruppen des Katalysators aber hemmt die Thermozersetzung und befördert die Wasserzersetzung.

Nickel wird im allgemeinen als die beste Katalysator für Methan-Wasserdampf-Reaktionen betrachtet. Bei vorliegender Arbeit kamen ausser Nickel, auch Kobalt, Kupfer und Eisen sowie Metalloxyde zur Verwendung.

Die Resultate sind in Tafel 8 zusammengestellt. Diese reduzierten Metalle sind alle wirksam; nächst Nickel ist Kobalt am wirksamsten. Von den Metalloxyden wurden Aluminiumoxyd, Chromoxyd, Wolframoxyd, Magnesiumoxyd, Kalziumoxyd, Uranoxyd, Kieselsäure, Thoriumoxyd, Zinnoxyd, Manganoxyd, Zinkoxyd, Vanadinoxyd, Bariumoxyd, benutzt. Die Oxyde haben meistens nur geringes katalytisches Vermögen für Methan-Wasserdampf-Reaktionen, ausserdem sind sie noch unbequem zu handhaben, da sie bei höherer Temperatur schmelzen und durch Methan leicht reduziert werden. Reine Kahlbaumsche Preparate wurden verwendet, u. zw. in Menge von 20–30 g.

Tafel 8.

Exp. Nr. a 25–a 66, Kat. Nr. A 1–A 41, Reak. Temp. 970°C., $H_2O/CH_4 = 2.0$, Gas. Ges. 5 lt/St.

Kat. Nr.	Bestandteil des Katalysators.	CO_2	CO	H_2	CH_4	Z.G.a.	Z.G.b.
A 1	Ni	2.0	21.3	72.3	4.4	84.2	94.5
A 2	Co	1.8	20.5	69.0	8.7	72.0	89.7
A 3	Fe	2.5	18.2	66.0	13.3	60.7	84.5
A 4	Cu	4.2	15.3	65.1	15.4	55.8	82.0
A 24	Cr_2O_3	1.7	18.7	70.1	9.5	68.0	88.2
A 25	Cr_2O_3	1.7	17.9	71.7	8.7	69.2	89 2
A 34	WO_3	4.0	11.9	52.3	31.8	33.4	62 2
A 37	Coks	3.8	11.5	51.1	33.6	31.2	61.3
A 29	MgO	3.8	9.5	44.9	41.8	24.2	53.5
A 31	CaO	6.4	9.6	53.4	30.6	34.4	63.5
A 32	U_3O_8	5.6	8.3	46.1	40.0	24.9	57.7
A 27	SiO_2	5.1	5.9	40.6	48.4	18.5	46.2
A 28	ThO_2	2.8	4.0	34.1	59.1	10.3	36.6
A 35	ZnO	4.7	3.6	35.1	56.6	12.8	38.3
A 38	MnO_2	4.2	3.0	42.4	50.4	14.9	45.7
A 33	V_2O_5	4.4	2.0	34.9	58.7	9.8	37.3
A 23	Al_2O_3	0.8	0.8	65.2	33.2	4.6	64.3
A 30	BaO	2.4	0.4	41.2	56.0	4.8	42.7
A 36	$ZnCrO_4$	3.6	2.8	41.4	52.2	10.9	44.2

Chromoxyd hat besondere Eigenschaften als andere Oxyde. Katalysator A 24 in Tafel 8, der aus Ammoniumbichromat durch Rösten hergestellt wird, und Katalysator A 25, der aus Natriumbichromat und Schwefel hergestellt wird, haben eine mässige Wirksamkeit und weisen verschiedene Eigenschaften auf, als andere schwer reduzierbare Oxyde. Zersetzungsgrad a ist der für Kohlenstoff und wird mit der Formel $(CO_2+CO)100/CO_2+CO+CH_4$ gezeigt und Zersetzungsgrad b ist der für Wasserstoff und wird mit der Formel $H_2\cdot100/H_2+CH_4$ gezeigt. Zersetzungsgrad a und b gehen meist mit einander parallel, allein Aluminiumoxyd und Bariumoxyd haben einen niederen Zersetzungsgrad a und einen höheren Zersetzungsgrad b. Daraus geht hervor, dass sie gute Katalysatoren für Thermozersetzung abgeben, aber für Wasserdampfzersetzung versagen.

Katalysator A 23 in Tafel 10 Quarzsand, 0.5–1.0 mm. Durchmesser, wird nach kurzer Zeit mit einem glänzenden Film Kohlenstoffs bedeckt. Bei Verwendung eines Katalysators mit geringem Zersetzungsvermögen a bildet sich geringe Menge eines teerartigen Stoffs, der hauptsächlich aus aromatischem Kohlenwasserstoff besteht.

Ich habe die oben erwähnten Katalysatoren allein jeden für sich verwendet. Durch Zusatz von schwer reduzierbaren Oxyden z.B. Silika, feuerfester Ziegel, Kaolin und Bimsstein wird die Wirksamkeit erhöht, wovon unten die Rede sein wird.

b) *Einfluss der Wasserdampfmenge.* Wie oben erwähnt, spielt die Wassermenge bei Methan-Wasserdampf-Reaktionen eine grosse Rolle. Grosse Menge Wasserdampf beschleunigt die Reaktion und gibt Kohlendioxyd in Menge, während kleine Menge Wasserdampf Kohlenoxyd vermehrt. Die Resultate der Reaktion mit grosser Menge Wasserdampf und ohne Katalysator, sind in Tafel 9 dargestellt. Die Zersetzung des Methans ist etwas besser als in Tafel 6, welche die Reaktionsresultate mit geringer Menge Wasserdampf zeigt. Aber es bilden sich schon freier Kohlenstoff und ungesätigter Kohlenwasserstoff.

Tafel 9.

Exp. Nr. b 59, $H_2O/CH_4 = 10$, ohne Kat., Gas. Ges. 5 lt/St.

Reak. Temp. °C.	CO_2	C_nH_m	CO	H_2	CH_4	Z.G.
500	1.2	0.5	0.2	0.0	98.1	1.4
600	1.2	0.4	0.3	0.0	98.1	1.5
700	1.2	0.5	0.6	0.0	97.7	1.8
800	1.4	0.3	3.0	14.9	80.4	5.2
900	2.2	0.2	6.2	27.7	63.7	11.6
1000	4.6	0.2	8.8	47.5	38.7	25.6

Tafel 10 zeigt die Wirkung guter Katalysatoren unter Zuführung grösserer Menge Wasserdampf wie in Tafel 7. Gasgeschwindigkeit ist 5.0 lt/St. Wenn man diese zwei Reaktionen mit einander vergleicht, so kann man den Einfluss der Katalysatoren auf einen Blick erkennen.

Tafel 10.

Exp. Nr. b 67, Kat. Nr. B 57, Gas. Ges. 5 lt/St., $H_2O/CH_4 = 10$.

Reak. Temp. °C.	CO_2	CO	H_2	CH_4	Z.G.	Volumzunahme; Mal.
500	18.6	1.4	76.6	3.4	85.4	3.5
600	18.6	3.0	77.7	0.7	96.4	4.4
700	18.2	3.2	78.1	0.5	97.7	4.3
800	17.2	4.4	77.9	0.5	97.7	4.3
900	16.8	5.4	77.4	0.4	98.2	4.4
1000	16.0	6.0	78.0	0.0	100.0	4.2

Abbildung 6 zeigt die Verhältnisse zwischen dem Zersetzungsgrad a des Methans und der Reaktionstemperatur in den Fällen, in denen man bald mit Katalysator, bald ohne ihn, sowie bald mit mehr, bald mit weniger Menge Wasserdampf gearbeitet hat.

Die Kurve in Abbildung 6 bedeutet:

A ohne Katalysator mit wenig Wasserdampf (Tafel 6)
B ohne Katalysator mit viel Wasserdampf (Tafel 9)
C mit Katalysator und wenig Wasserdampf (Tafel 7)
D mit Katalysator und viel Wasserdampf (Tafel 10)
E mit Nickel allein und viel Wasserdampf (Tafel 14)
F Vermögenskurve des Nickels.

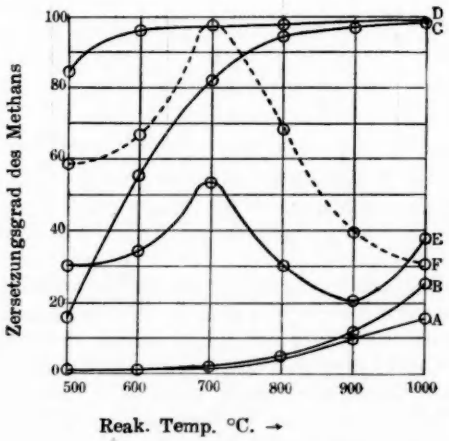


Abb. 6. Die Kurve Zersetzungsgrad des Methans.

Tafel 11 und 12 zeigen die Resultate der Experimente, die ich zur genaueren Verfolgung der Einflusse des Wasserdampfs auf Methan-

Wasserdampf-Reaktionen bei 600°C. vorgenommen habe. In Tafel 11 ist die Methangeschwindigkeit konstant und die Menge des Wasserdampfes verändert, so dass die Geschwindigkeit des letzteren sich verändert. In Tafel 12 ändert sich die Geschwindigkeit des Wasserdampf und ist die gesamt Geschwindigkeit des Ganzen konstant. Als Katalysatoren wurde Nickel, Alumina und Porzellan verwendet.

Tafel 11.

Exp. Nr. b 49, Kat. Nr. B 39, Reak. Temp. 600°C. Gas. Ges. 5 lt/St.

H_2O/CH_4	CO_2	H_2	CH_4	CO	Z.G.
17.5	19.8	79.2	0.0	1.0	100.0
10.5	19.2	78.9	0.1	1.8	99.5
7.5	18.5	77.8	0.5	3.2	96.5
5.1	17.2	76.9	0.9	5.0	96.1
3.3	16.6	75.7	2.2	5.5	91.0
2.0	12.3	69.0	11.7	7.0	62.2
0.5	2.0	48.4	47.8	1.8	7.5

Tafel 12.

Exp. Nr. b 47, Kat. Nr. B 39, Reak. Temp. 600°C.

CH_4 lt/St.	H_2O/CH_4	CO_2	CO	H_2	CH_4	Z.G.
2.0	20.0	19.2	1.4	79 4	0.0	100.0
3.6	11.0	19 3	2.4	78.2	0.1	99.5
5.0	7.5	18.7	2.6	78.1	0.6	97.2
6.6	5.3	16.2	5.3	77.8	0.7	96.9
11.0	3.6	14 3	8.2	75.9	1.6	93.3

c) *Einfluss der Temperatur und des Drucks auf die Reaktionen.* Die Wirkung der Temperatur auf die Reaktionen ist, theoretisch und experimentel, aus der oben angegebenen Tafel der Gleichgewichtskonstanten zu ersehen.

Wenn der Reaktionsdruck annimmt, so fällt die Reaktionstemperatur, da bei der Reaktion eine Vergrösserung des Volumes entsteht.

Tafel 13 zeigt die Resultate der Experimente unter dem Druck resp. 760, 400, 200, 100 und 50 mm. der Quecksilbersäule. Einfluss des Drucks wird unter 200 mm. Quecksilbersäule sichtbar. Unter 500°C. zersetzt sich Methan in Kohlenoxyd und Wasserstoff. Abbildung 7 zeigt die Verhältnisse zwischen Druck und Zersetzungsgrad a des Methans. Gasgeschwindigkeit ist 5.0 lt/St. $H_2O/CH_4 = 2.0$. Als Katalysator wurde Nickel-Alumina verwendet. Da dieser Katalysator nur mittelmässiges Beschleunigungsvermögen hat, so sind die Resultate verhältnismässig schlecht, bei Verwendung besserer Katalysatoren aber kann man schon auf bessere Resultate rechnen.

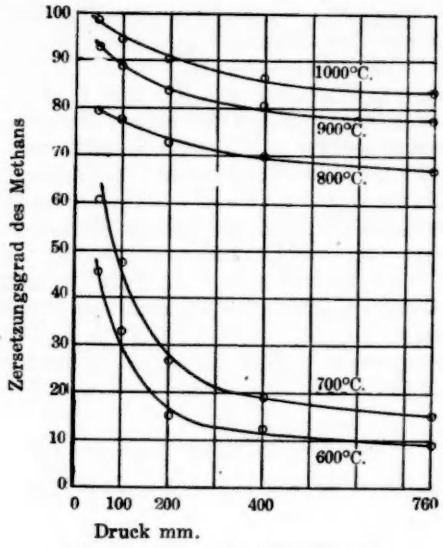


Abb. 7. Druck und Zersetzungsgrad.

Tafel 13.

Exp. Nr. a 101–a 150, Kat. Nr. A 47, Gas. Ges. 5 lt/St., $H_2O/CH_4 = 2.0$.

Reak. Temp. °C	Druck mm. Hg	CO_2	CO	H_2	CH_4	Z.G.
600	50	5.0	13.5	59.5	22.0	45.7
,,	100	5.0	10.4	53.3	31.3	33.6
,,	200	4.4	5.0	34.2	56.4	14.8
,,	400	4.2	4.7	30.7	60.4	12.8
,,	760	3.6	3.4	22.7	70.3	9.1
700	50	1.7	19.8	64.6	13.9	60.7
,,	100	1.0	18.3	57.2	23.5	45.5
,,	200	3.0	10.7	45.3	41.0	25.0
,,	400	3.7	7.8	40.5	48.0	19.3
,,	760	4.2	5.6	34.3	55.8	14.9
800	50	2.0	21.0	71.1	5.9	79.5
,,	100	2.0	22.0	69.0	7.0	77.3
,,	200	1.7	20.8	68.8	8.7	72.2
,,	400	1.0	21.0	68.5	9.5	69.8
,,	760	1.9	20.0	67.1	11.0	66.5
900	50	0.3	24.5	73.5	1.8	93.3
,,	100	0.3	24.4	72.1	3.2	88.5
,,	200	0.0	24.0	71.5	4.5	84.3
,,	400	0.0	22.8	71.7	5.5	80.5
,,	760	0.0	22.6	70.9	6.5	77.7
1000	50	0.0	24.8	75.0	0.2	99.0
,,	100	0.0	24.2	74.5	1.3	95.0
,,	200	0.0	24.0	73.6	2.4	91.0
,,	400	0.0	23.2	73.3	3.5	86.7
,,	760	0.0	22.0	73.4	4.4	83.5

d) *Nickel-Katalysator.* Unter den ausgeführten vielen Experimenten, hat sich das Nickel als der beste Katalysator bewährt, und welches ich im folgenden gedenke, u. zw.

1. Nickel allein. 2. Promotor und Träger 3. Katalysator aus zwei Elementen. 4. Beifügungsmenge des Promotors, Konzentration und Korngrösse des Katalysators. 5. Kontaktdauer. 6. Röstungs- und Reduktions-Temperatur. 7. Haltbarkeit des Katalysators. 8. Katalysator mit Alkalien.

1. Anwendung des Nickels allein. Wenn man Nickel allein gebraucht, so sinkt die Wirkung des Katalysators bedeutend durch Semisinterung herab. Da die Reaktion eine endothermische und oberfläche ist, so ist die Wirkung eine ganz andere als die der Reaktionswärme.

Die Resultate bei Anwendung des Nickels ohne Träger und Promotor, sind in Tafel 14 zusammengestellt. Das Nickel wurde hierbei aus Nickelnitrat und Alkali hergestellt, indem das so erhaltene Nickelhydroxyd bei 500°C. geröstet und bei 300°C. mit Wasserstoff reduziert wurde.

Tafel 14.

Exp. Nr. b 23, Kat. Nr. B 16, Gas. Ges. 5 lt/St., $H_2O/CH_4 = 10.0$.

Reakt. Temp. °C	CO_2	CO	H_2	CH_4	Z.G.
500	14.0	0.8	51.0	34.2	30.2
600	13.5	0.6	58.4	27.5	33.9
700	16.5	1.4	66.4	15.7	53.3
800	11.4	3.8	57.0	27.8	35.3
900	8.8	3.0	41.1	47.1	20.0
1000	10.7	5.4	57.6	26.3	37.9

Zersetzungsgrad des Methans steigt mit Temperaturerhöhung, aber bei 800°C. sinkt er plötzlich, bei 900°C. hat er die niedrigsten Werte und über 1000°C. steigt er wieder langsam auf. Diese Erscheinung die auf den ersten Blick unregelmässig erscheint, führt sich, bei genauerer Beobachtung, auf folgenden Ursachen zurück.

Die Reaktion schreitet mit der Steigerung der Temperatur fort, aber an einem Punkt vermindert sich das katalytische Vermögen des Katalysators plötzlich und der Zersetzungsgrad sinkt herab, obgleich die Temperatur immer höher steigert, bleibt das katalytische Vermögen am niedrigsten. Die langsame Steigerung des Zersetzungsgrades ist der Wirkung der Wärme, nicht der des Katalysators, zuzuschreiben. Das katalytische Vermögen hat bei 700°C. den maximalen Wert und sinkt mit der Steigerung der Temperatur wieder herab. Abbildung 6 zeigt graphisch dieses Verhältnis. Kurve E zeigt den Zersetzungsgrad der oben erwähnten Reaktion, Tafel 14 mit Nickel Katalysator. Kurve A das Resultat ohne Katalysator, Tafel 6, Kurve F Vermögenskurve des Katalysators, die sich aus Kurve E und A ergibt. Man kann die Ergebnisse des Experimentes aus Kurve A, E, F erklären.

Verminderung der Oberfläche durch Halbsinterung verursacht

schnelle Verminderung des katalytischen Vermögens des Nickels. Diese Tatsache ist aus folgenden Experimenten deutlich zu ersehen. Wenn man die Verwandlung des Katalysators in einem durchsichtigen Quartzrohr beobachtet: das reduzierte Nickel zeigt bei 300°C. eine schwarze Farbe, bei 500°C. eine graue, bei 600°C. koaguliert es allmählich zu grauen Körnern, welche metallisch glänzende Partikeln haben. Diese Erscheinung schreitet mit der Temperatursteigerung fort. Bei 1000°C. tritt das Nickel als grosskörniges Metall hervor. Dieses hat ziemlich gleiches Vermögen wie das marktmässige körnige Nickel. Die Temperatur, wo reduziertes Pulver des Nickels zur Koagulierung und Halbsinterung kommt, ist verhältnismässig niedrig, schon bei 600°C. vermindert sich das Vermögen des Katalysators, der Zersetzungsgrad des Methans aber erst nach längerer Zeit.

Tafel 15 und Abbildung 8 erklären die Tatsache.

Tafel 15.

Exp. Nr. b 24, Kat. Nr. B 16, Gas. Ges. 5 lt/St., Reak. Temp. 600°C., $H_2O/CH_4 = 10.0$.

Verlauf (Min.)	CO_2	CO	H_2	CH_4	Z.G.
60	15.0	1.2	60.8	23.0	41.3
90	15.0	1.0	59 5	24.5	39.8
120	14.4	1.0	56.2	28.4	35.1
150	14.8	1.0	58.3	25.9	37.9
180	14.8	1.1	60.0	24.1	39.9
210	13.8	1.0	52.6	32.6	31.2
240	12.5	1.0	55.2	31.3	30.1
270	12.6	0.8	51.2	35.4	27.4
300	13.1	1.0	54.9	31.0	31.2
330	11.0	0.8	49.9	38.3	23.5
360	11.8	1.1	49.4	37.7	25.5
420	12.6	1.0	51.7	34.7	28.2

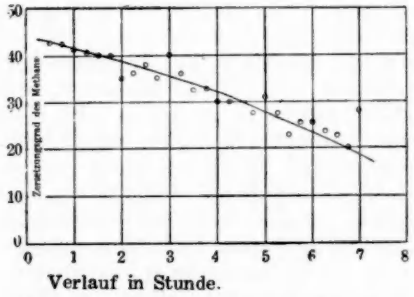


Abb. 8. Verminderung des katalytischen Vermögens des Nickels.

Katalysator mit geringem Vermögen gibt schwankende und unbestimmte Resultate (Tafel 15). Wenn man Nickel allein gebraucht, kann man eine Verminderung des katalytischen Vermögens infolge einer langdauernden Temperatursteigerung nicht vermeiden. Um einer Verminderung des katalytischen Vermögens vorzubeugen, versuchte ich die Anwendung des Promotors und Trägers. Der Zusatz dieser Materien hat gewissermassen meiner Erwartung entsprochen.

2. Promotor und Träger. Die Wirkung des Promotors auf den Katalysator ist eine günstige; insbesondere Magnesiumoxyd, Aluminiumoxyd, Kieselsäure und Chromoxyd u.s.w. haben in zweckmässiger Menge einen wichtigen Einfluss entfaltet. Tafel 16 zeigt die Resultate, die sich bei Gebrauch des Nickelkatalysators, und der schwer reduzierbaren Oxyde in verschiedenen Mengen-Verhältnisse ergeben haben; Reaktionstemperatur, 970°C., $CH_4/H_2O=2.0$. Dabei wurde Nickeloxyd Pulver mit dem anderen Oxyd Pulver vermischt, das Ergebnis war aber besser als mit Nickel allein.

Tafel 16.

Exp. Nr. a 70–a 100, Kat. Nr. A 45–A 67, Reak. Temp. 970°C., Gas. 5 lt/St., $H_2O/CH = 2.0$.

Kat. Nr.	Bestandteil des Katalysators $Ni+Al_2O_3$ (Mol)	CO_2	CO	H_2	CH_4	Z.G.
A 45	0.9 : 0.1	2.8	20.2	75.3	1.7	93.0
A 46	0.7 : 0.3	0.8	24.6	73.5	1.1	95.8
A 47	0.5 : 0.5	4.4	20.1	73.6	1.9	92.8
A 48	0.3 : 0.7	0.7	23.4	74.0	1.9	92.8
A 49	0.1 : 0.9	0.6	23.5	74.2	1.7	93.5
	Ni : MgO					
A 51	0.9 : 0.1	1.1	22.1	75.3	1.5	94.0
A 52	0.7 : 0.3	0.6	23.7	75.2	0.5	94.0
A 53	0.5 : 0.5	2.0	21.5	73.3	3.2	91.2
A 54	0.3 : 0.7	0.4	23.0	74.3	2.3	91.0
A 55	0.1 : 0.9	1.6	23.1	73.3	2.0	92.5
	Ni : SiO_2					
A 60	0.1 : 0.9	0.8	22.1	73.3	3.8	85.2
	Ni : Cr_2O_3					
A 65	0.1 : 0.9	1.6	21.8	72.0	4.6	83.5
	Ni :					
A 67	10% Ni	2.8	22.4	73.3	1.5	94.5

Die Anwendung eines richtigen Trägers befördert ferner die leichte Formgebung des Katalysators, Verhütung der Halbsinterung und so kann man feuerfestere und bequemere dauerhaftere Katalysatoren gewinnen. Als Träger muss man feuerfeste und poröse Materien, wie Bimsstein, Porzellan, Kaolin, feuerfesten Ziegel usw. erwählen. Da aber diese Materie in ihren Eigenschaften und Komponenten sehr verschieden sind, so lässt sich etwas Allgemeingültiges darüber nicht sagen. Bimsstein ist poröse aber nicht feuerfest und kann deshalb nur bei niederer Temperatur in Betracht kommen, bei einer höheren Temperatur versagt er ganz und gar. Porzellanscherben und feuerfester Ziegel kommen in Frage, aber sie passen nicht zu Formgebung und Anhaften des Nickels. Die Mazerationsmethode in Salzlösung ist nicht am Platz, weil bei der Trocknung die Konzentration der Oberfläche des Katalysators zu gross wird und ein Film der Metalle sich bildet. Der Katalysator mit Kaolin und Nickelhydroxyd unter Mischung mit Wasser und Formgebung

ist der wirksamste unter den Niederschlagskatalysatoren. Dagegen von den Röstungskatalysatoren entfaltet der aus Nickel und Chromoxyd die beste Wirkung.

Andere Materien z.B. Alumina, Kieselsäure, Magnesia können in Frage kommen, nur die Formgebung ist bei ihnen etwas schwierig. Tafel 17 zeigt die Resultate der Experimente, in denen ich dem Nickel als Katalysator Alumina, Magnesia, Kieselsäure und Chromoxyd als Promotor und Bimsstein als Träger beigegeben habe. Diese bilden zusammen mit Lösungsgemischen der Nitraten Niederschläge.

Tafel 17.

Ges. Gas. 5 lt/St., $H_2O/CH_4 = 10$–7, Ni-Katalysator.

Exp. Nr.	Kat. Nr.	Träger	Promotor	Reak. Temp. °C	CO_2	CO	H_2	CH_4	Z.G.
b 22	B 15	Bimsstein	Al_2O_3	500	18.2	3.1	75.9	2.8	88.3
				600	18.0	4.0	76.9	1.1	95.8
				700	17.1	4.5	78.0	0.4	98.0
b 38	B 30	Feuerfester Ziegel	Al_2O_3	500	19.2	0.9	76.4	3.5	85.3
				600	17.6	3.1	76.5	2.8	88.0
				700	18.6	2.6	77.8	1.0	95.5
b 43	B 37	Porzellan	Al_2O_3	500	19.4	1.8	76.7	2.1	90.8
				600	18.2	3.1	77.5	1.2	94.7
				700	19.2	3.0	77.3	0.5	98.5
b 66	B 58	Kaolin	Al_2O_3	500	19.2	1.2	76.2	3.4	89.3
				600	18.9	3.0	77.3	0.8	96.5
				700	18.2	3.0	78.3	0.5	97.7
				800	17.2	4.2	78.4	0.2	99.0
				900	15.5	6.0	78.5	0.0	100.0
				1000	15.5	7.4	77.1	0.0	100.0
b 72	B 55	Kaolin	MgO	500	19.5	1.4	74.4	4.7	81.5
				600	19.6	1.8	77.3	1.3	94.2
				700	19.3	2.0	77.8	0.9	96.0
				800	18.8	2.0	78.5	0.8	96.3
				900	18.3	2.8	78.1	0.8	96.5
				1000	18.2	4.1	76.9	0.7	97.0
b 76	B 40	Kaolin	Cr_2O_3	500	18.7	1.0	75.6	4.7	80.8
				600	18.8	2.1	77.8	1.3	94.0
				700	18.6	2.9	77.7	0.8	96.5
				800	16.6	5.1	77.6	0.7	96.8
				900	15.5	6.9	77.1	0.5	98.0
				1000	15.0	7.6	76.9	0.5	98.0
b 14	B 9	Bimsstein	Fe_2O_3	500	17.4	1.8	68.7	12.1	61.3
				600	16.7	4.4	76.1	2.8	88.3
				700	13.6	7.0	76.8	2.6	88.8

3. Katalysator besteht aus zwei Metallen. Weiter studierte ich die Wirkung Nickel-Katalysators mit Kupfer, Eisen, Silber, Kobalt, Mangan und Chrom auf Methan-Wasserdampf-Reaktion. Doch konnte ich keinen bedeutenden Einfluss beobachten. Die erhaltenen Resultate sind in Tafel 18 zusammengestellt. Dabei fand ich aber einen feuerbeständigen Katalysator, der, wie unten erwähnt wird, durch Röstungs- und Reduktions-Temperatur wenig beeinträchtigt wird, Reaktionstemperatur 1000–1100°C. Methangeschwindigkeit 100 lt/St. Verhältnis Methans zu Wasser ist 2.0.

4. Menge des Promotors, Konzentration und Korngrösse des Katalysators. Wenn man die Menge der Alumina des Katalysators in Alumina-Nickel Reihe verändert, so ergeben sich interessante Resultate. Es stellte sich nähmlich heraus, dass es eine optimale Beifügungsmenge des Promotors gibt, Tafel 19. Der Katalysator wird folgendermassen hergestellt; die Lösung der Nitrate des Nickels und Aluminiums wird in gewissem Verhältniss vom feuerfesten Ziegel absorbiert und getrocknet und geröstet und mit Wasserstoff sorgfältig reduziert.

Tafel 18.

Gas. Ges. 70 lt/St., Reak. Temp. 1000°C., $H_2O/CH_4 = 2.0$, Ni-Katalysator.

Exp. Nr.	Kat. Nr.	Träger	Promotor	Reak. Temp. °C	CO_2	CO	H_2	CH_4	Z G.
g 25	G 1	Kaolin	Al_2O_3	880	3.8	20.5	74.6	1.1	95.8
g 22	G 2	Kaolin	Bauxite	990	5.5	17.6	73.1	3.8	86.0
g 40	G 3	Kaolin	Fe_2O_3	800	5.2	16.2	71.7	6.7	76.0
g 34	G 5	Kaolin	Ag	1000	3.8	18.6	72 6	0.9	96.2
g 37	G 6	Kaolin	MnO_2	950	4.4	17.4	71.0	7.2	75.2
g 36	G 8	Kaolin	Cu	1100	8.2	17.4	64.8	9.3	73.5
g 33	G 12	Kaolin	Co	990	7.3	15.9	76.0	0.8	96.5
g 19	G 13	ohne	Bauxite	1000	4.6	20.0	74.4	1.0	95.0

Tafel 19.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 7$.

Exp. Nr.	Kat. Nr.	Katalysator $Ni : Al_2O_3$ mol.	Reak. Temp. °C	CO_2	CO	H_2	CH_4	Z.G.
b 41	B 32	1 : 0.500	500	17.2	1.4	68.1	13.3	58.3
b 36	B 28	1 : 0.250	500	16.7	2 1	71.4	9.8	65.7
b 35	B 27	1 : 0.100	500	16.6	0.8	73.5	9.1	65.7
b 34	B 26	1 : 0.050	500	17.8	1.3	71.9	9.0	68.0
b 38	B 30	1 : 0.025	500	19.2	0.9	76.4	3.5	85.2

Tafel 19.—(fort.)

Exp. Nr.	Kat. Nr.	Katalysator Ni : Al_2O_3 mol.	Reak. Temp. °C	CO_2	CO	H_2	CH_4	Z.G.
b 40	B 33	1 : 0.010	500	17.4	1.8	72.7	8.1	70.0
b 37	B 29	1 : 0.005	500	15.8	0.8	69.7	13.7	54.7
b 39	B 31	1 : 0.000	500	17.2	1.5	69.6	11.7	61.4
b 41	B 32	1 : 0.500	600	18.8	1.7	74.8	4.7	81.3
b 36	B 28	1 : 0.250	600	18.6	1.4	73.6	6.4	75.7
b 35	B 27	1 : 0.100	600	18.9	1.2	74.7	5.2	79.5
b 34	B 26	1 : 0.050	600	18.7	1.6	73.9	5.8	78.0
b 38	B 30	1 : 0.025	600	17.7	3.1	76.7	2.5	89.2
b 40	B 33	1 : 0.010	600	18.9	1.8	75.8	3.5	85.5
b 37	B 29	1 : 0.005	600	18.2	1.7	73.4	6.7	74.8
b 39	B 31	1 : 0.000	600	17.6	1.8	69.6	11.0	63.8
b 41	B 32	1 : 0.500	700	19.6	2.2	75.6	2.6	89.3
b 36	B 28	1 : 0.250	700	18.6	2.0	76.6	2.8	88.0
b 35	B 27	1 : 0.100	700	18.6	2.0	77.5	1.9	91.5
b 34	B 26	1 : 0.050	700	18.7	3.0	76.5	1.8	92.1
b 38	B 30	1 : 0.025	700	18.6	2.6	77.8	1.0	95.5
b 40	B 33	1 : 0.010	700	18.9	2.6	76.7	1.8	92.3
b 37	B 29	1 : 0.005	700	18.2	2.1	74.7	5.0	80.2
b 39	B 31	1 : 0.000	700	17.1	3.4	73.8	5.7	78.2

Zur Bestimmung der optimalen Konzentration des Katalysators auf dem Träger habe ich Experimente angestellt, die in der Tafel 20 angegeben sind. Bei Konzentration des Nickels über 7–8% der Gewichte des Trägers, hat der Katalysator ein sehr wirksames Vermögen, aber unter 7% sinkt das Vermögen deutlich herab, während bei einer Konzentration über 10% er in seiner Wirkung kaum beeinnflusst wird. So befindet sich die optimale Konzentration des Katalysators in der Nähe von 10%: Grosse Konzentration bei Bimsstein, ferner feuerfestem Ziegel, hat einen schlechten Einfluss, auf den Träger, da eine Sinterung des Metalls leicht auf der Oberfläche des Katalysators geschieht. Die optimale Konzentration bei Porzellan ist 7% und die bei Kaolin ist 10%. Bei Porzellan ist, je nach der Darstellungsweise des Katalysators, die Konzentration an der Oberfläche grösser als im Innern. Der Oberflächenzustand des Trägers spielt hierbei eine wichtige Rolle, so dass man die optimale Konzentration des Katalysators nicht so einfach bestimmen kann.

Tafel 20.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 7$.

Exp. Nr.	Kat. Nr.	Konzentration %	Reakt. Temp. °C	CO_2	CO	H_2	CH_4	Z.G.
Träger: Bimsstein.								
b 45	B 35	1.6	500	17.5	1.5	72.2	8.8	68.0
b 42	B 34	3.0	500	18.4	1.4	72 3	7.9	71.5
b 43	B 37	7.0	500	19.4	1.8	77.2	1.6	93.0
b 44	B 38	16.0	500	20.1	1.5	76.6	1.8	92.0
b 45	B 35	1.6	600	18.0	2.8	73.4	5.8	78.1
b 42	B 34	3.0	600	18.2	2.3	73.9	5.6	78.5
b 43	B 37	7.0	600	18.2	3.1	77.8	0.9	95.9
b 44	B 38	16.0	600	19.0	2.2	78.2	0.6	97.0
b 45	B 35	1.6	700	18.0	3.7	73.9	4.4	83.1
b 42	B 34	3.0	700	17.6	2.7	76.3	3.4	85.7
b 43	B 37	7.0	700	19.0	3.0	77.7	0.3	98.7
b 44	B 38	16.0	700	18.2	3.6	78.2	0.0	100.0
Träger: Feuerfester Ziegel.								
b 54	B 59	5.0	500	18.4	1.6	72.4	7.6	72.4
b 55	B 60	8.0	500	18.7	1.5	77.2	2.6	83.5
b 57	B 58	9.8	500	19.8	1.2	77.9	1.1	95.0
b 56	B 61	12.2	500	19.4	1.1	78.5	1.0	95.5
b 54	B 59	5.0	600	18.0	2.0	78.8	11.2	94.7
b 55	B 60	8.0	600	19.0	1.8	78.2	1.0	95.5
b 57	B 58	9.8	600	19.6	2.2	77.6	0.6	97.4
b 56	B 61	12.2	600	19.4	1.8	78.3	0.5	97.7
b 54	B 59	5.0	700	18.7	3.3	77.0	1.0	95.7
b 55	B 60	8.0	700	18.0	2.2	79.2	0.6	97.0
b 57	B 58	9.8	700	18.2	2.8	78.7	0.3	98.5
b 56	B 61	12.2	700	18.5	2.7	78.6	0.2	99.0

Der Katalysator durch Niederschlagsmethode hat homogene Struktur an der Oberfläche und im Innern, so dass die Konzentration leicht bestimmt wird. Je kleiner die Körner des Katalysators ist, desto grösser ist deren Oberfläche, desto besser die Wirkung, zugleich wird aber Widerstand gegen den Gaszug grösser. Tafel 21 zeigt die Resultate mit verschiedener Körngrösse des Katalysators.

Tafel 21.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 10$.

Exp. Nr.	Kat. Nr.	Reak. Temp. °C.	CO_2	CO	H_2	CH_4	Z.G.
b 75	B 58	500	18.7	1.5	73.9	5.9	77.5
b 74	B′ 58	500	19.0	1.6	76.4	3.0	86.9
b 65	B″ 58	500	18.8	1.9	76.4	2.9	87.7
b 75	B 58	600	19.1	1.9	77.4	1.6	92.8
b 74	B′ 58	600	19.0	2.6	78.5	0.7	96.7
b 65	B″ 58	600	18.6	2.6	78.3	0.5	97.7
b 75	B 58	700	17.8	2.8	78.0	1.4	93.5
b 65	B′ 58	700	18.3	3.0	78.3	0.4	98.5
b 65	B″ 58	700	18.4	3.6	77.7	0.3	98.7

Korngrösse B 58 . . . . 10 mm / 10 mm Zylinder.
B′ 58 . . . . 3 mm / 4 mm „
B″ 58 . . . . 2 mm / 3 mm „

5. Kontaktdauer. Sie ist ein sehr wichtiger Faktor für den Fortgang der Reaktion, und wird durch vielen Bedingungen z.B. Katalysator, Temperatur und Gasgeschwindigkeit usw. bedingt. Zur Aufklärung dieser Punkte habe ich folgende zwei Experimente ausgeführt. Einmal veränderte ich die Menge der Katalysatoren, die zu Kaolin-Alumina-Nickel Reihe gehören, wobei die Geschwindigkeit des Gases konstant blieb. Das zweite Mal versuchte ich die Experimente bei gleicher Menge des Katalysators und verschiedener Menge der Wasserdämpfe. Nachfolgende Formel zeigt die Kontaktdauer.

$$\text{Kontaktdauer (Sek.)} = \frac{\text{Volum des Katalysators in c.c.}}{\text{Methan Volum pro Stunde in c.c.}} \times 3600$$

Bei 700°C. beträgt sie, nach der Gleichung $CH_4 + 2H_2O = CO_2 + 4H_2$, 25–20 Sekunde und 10–15 Sekunde bei 900°C. nach der Gleichung $CH_4 + H_2O = CO + 3H_2$.

Tafel 22 und 23 sind die Resultate, und Abbildung 9 zeigt die Verhältnisse zwischen Kontaktdauer und unverändertem Methan im Reaktionsgas.

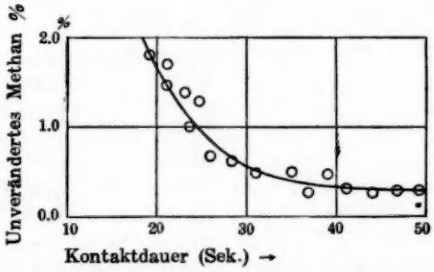


Abbildung 9. Kontaktdauer und unverändertes Methan.

Tafel 22.

Kat. Nr. B 58., Gas Ges. 5 lt/St., $H_2O/CH_4 = 10$.

Exp. Nr.	Kat. Gewicht g.	Kontakt-Dauer (Sek.)	Reaktions-Temp. °C.	CO_2	CO	H_2	CH_4	Z.G.
b 68	10	12.3	500	17.4	1.4	68.0	13.2	58.8
			600	17.8	2.4	71.7	8.1	71.2
			700	17.0	4.0	73.4	5.5	79.2
b 69	20	24.6	500	19.5	1.1	73.2	6.2	75.5
			600	18.4	2.4	77.7	1.5	93.2
			700	17.6	4.4	76.7	1.3	94.5
b 66	30	37.0	500	19.3	0.8	76.9	3.0	87.0
			600	18.9	3.0	77.3	0.8	96.5
			700	18.3	3.0	78.1	0.5	97.7
b 70	40	49.3	500	19.4	2.1	76.9	1 6	91.0
			600	19.1	2.2	78.1	0.6	97.2
			700	18 5	3.4	77.8	0 3	98.5

Tafel 23.

Exp. Nr. b 73, Kat. Nr. B 58, Reak. Temp. 600°C., $H_2O/CH_4 = 7$.

Gas Geschwindigkeit (Lt/St)	Kontakt Dauer (Sek.)	CO_2	CO	H_2	CH_4	Z.G.
4.2	44	17.5	5.0	77.1	0.4	98.0
4.8	39	18.2	3.3	78.0	0.5	97.7
5.3	35	17.8	4.1	77.4	0.7	96.7
6.0	31	17.9	3.8	77.6	0.7	96.7
7.2	26	17.4	4.4	77.3	0.9	96.0
8.0	23	18.0	3.6	76.7	1.7	92.7
8.9	21	17.8	3.5	76.5	2.2	90.6
9.9	19	17.9	3.6	76.5	2.2	90.6

6. Röstungs- und Reduktions-Temperatur des Katalysators. Im allgemeinen ist die Röstungs- und Reduktions-Temperatur des Katalysators bei der Nickel-Kaolin-Alumina Reihe sehr wichtig. Diese Tatsache ist aus der Tafel 24 deutlich zu ersehen. Der bei 400, 500 resp. 600°C. geröstete Katalysator wird bei 300°C. durch Wasserstoff reduziert, bei 350°C. ist er schon wirksam; bei 600°C. beträgt der Zersetzungsgrad 97.7. Die Erhöhung der Röstungstemperatur steigert die Reduktionstemperatur und setzt das Vermögen herab.

Der Katalysator, geröstet bei 900–1000°C., kann nicht unter 600–700°C. reduziert werden. Er verliert auch unter niedriger Temperatur die katalytische Wirkung. Diese Erscheinung beruht auf der Bildung inaktiver Verbindungen (Silikat und Aluminat) infolge einer Wirkung des Nickels auf den Träger. Zur Aufklärung dieser Vorgänge machte ich die Experimente, wie in Tafel 25 gezeigt, durch Gebrauch von Nickel Silikat (meta) und Aluminat (meta) als Katalysator. Diese Katalysatoren sind unter niedriger Temperatur unwirksam, bei höher Tempe-

rature aber sind sie wirksam. Abbildung 10 zeigt die Verhältnisse zwischen der Temperatur und dem Zersetzungsgrad des Katalysators bei verschiedener Röstungstemperatur.

Tafel 24.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 10$, Katalysator 30 g.

Exp. Nr.	Kat. Nr.	Röst-Temp.	Reduk. Temp.	Reak. Temp.	CO_2	CO	H_2	CH_4	Z.G.
b 83	B 46	400	300	300	1.2	0.8	2.7	95.3	2.1
				350	10.6	1.3	35.7	52.4	18.3
				400	16.8	0.9	61.9	20.4	45.1
				500	19.1	1.3	74.1	5.5	79.3
				600	19.0	3.4	77.1	0.5	97.8
				700	17.7	4.5	77.6	0.2	98.9
				800	16.3	5.5	78.0	0.2	99.3
				900	15.9	6.4	77.7	0.0	100.0
				1000	14.8	7.2	78.0	0.0	100.0
b 84	B 47	500	300	350	8.5	0.8	33.7	57.0	16.3
				400	11.1	1.0	40.9	47.0	20 5
				500	18.4	1.4	76.8	3.4	85.5
				600	18.5	2.8	77.0	1.7	92.6
				700	17.8	3.8	77.3	1.1	95.2
				800	16.0	5.4	77.7	0.9	96.0
				900	15.9	6.1	77.4	0.6	97.3
				1000	13.0	9.4	77.4	0.4	98 2
b 92	B 48	600	300	350	7.2	0.8	30.9	61.1	10.8
				400	15.1	1.0	58.5	25.4	38.8
				500	18.9	2.3	73.9	4.9	81.2
				600	18.7	2.8	76.9	1.6	93.0
				700	17.7	3.4	78.2	0.7	97.0
				800	17.1	5.4	77 1	0.4	98.2
				900	15.8	5.7	78.1	0.4	98.2
				1000	15.5	6.3	78.2	0.0	100.0
b 87	B 49	700	300	350	2.4	1.4	6.5	89.7	4.1
				400	7.6	1.2	28.4	63.4	11.9
				500	18.3	1.2	69.3	11.2	63.5
				600	18.2	3.0	77.0	1.8	92.2
				700	18.0	3.5	77.4	1.1	95.0
				800	16.4	4.8	78.1	0.7	96 7
				900	16.2	5.5	77.8	0 5	97.5
				1000	15.4	6.8	77.5	0.3	98.5
b 86	B 50	800	400	400	5.7	0.8	23.6	69.9	8 5
				500	14.2	1.0	56.7	28.1	35.1
				600	17.4	1.7	69.6	11.3	62.8
				700	17.1	3.8	78.0	1.1	94.8
				800	16.9	4.6	77.8	0.7	96.8
				900	16.7	5.0	77.8	0.5	97.7
				1000	14.0	8.0	77.7	0.3	98.5
b 94	B 51	900	600	600	10.5	1.0	38.4	50.1	18.6
				700	16.0	2.6	73.3	8.1	68.2
				800	17.4	3.7	77.1	1.8	92.2
				900	15.3	7.5	76.2	1 0	95.7
				1000	16.3	4.9	77.9	0.9	95.9
b 88	B 52	1000	700	700	16.3	2.5	68.3	12.9	59.3
				800	16.0	5.4	76.8	1 8	92.2
				900	15.6	5.5	78.0	0.9	96 0
				1000	14.7	6.4	78.2	0.7	96.8

Tafel 25.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 7$.

Exp. Nr.	Katalysator.	Reak. Temp. °C.	CO_2	CO	H_2	CH_4	Z.G.
f 17	Nickel- + meta-Silikat F 11	600	1.0	0.5	0.0	96 5	1.5
		700	3.0	0.0	1.3	95.7	3.0
		800	13.5	1.5	35.0	50.0	23.1
		900	14.2	3.1	49.3	35 5	32.8
		1000	14.6	7.4	73.7	4.3	33.8
f 13	Nickel-Aluminat F 13	610	7 2	0.6	27.7	65.0	10.7
		700	10.2	2.4	50.1	36.3	25.8
		800	12.1	5.8	68.7	13.4	57.3
		900	12.8	7.2	74.4	5.6	78.3
		990	12.6	7.8	75.6	4.0	83.8

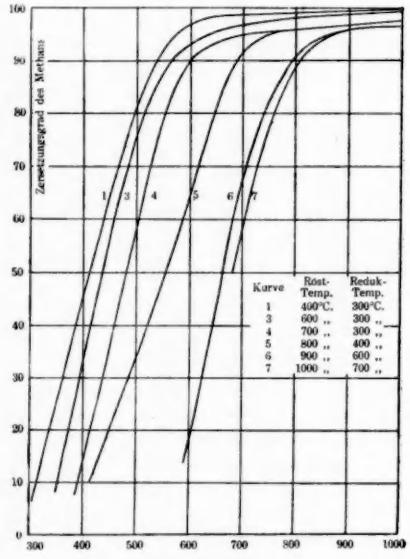


Abb. 10. Röstungstemperatur und Zersetzungsgrad des Methans.

Metalloxyde, die kein Wirkungsvermögen haben, werden aktiv, wenn sie bei über 800°C. durch Methan reduziert werden. Es gibt auch Katalysatoren, welche durch Röstungstemperature nicht beeinflusst werden, z.B. derjenige, der aus Nickelbichromat durch Hitzezersetzung hergestellt wird. Seine Wirksamkeit ist zwar etwas geringer aber sie sind feuerfest. Tafel 26 zeigt diese Verhältnisse.

Tafel 26.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 10$.

Exp. Nr.	Kat. Nr.	Röst-Temp. °C.	Reak. Temp. °C.	CO_2	CO	H_2	CH_4	Z.G.
b 80	B 52	1000	800	1.2	0.8	2.5	95.5	2.1
			900	1.8	4.4	15.6	78.2	7.4
			1000	16.0	5.8	75.5	2.7	88.9
			1100	15.9	5.7	77.6	0.7	96.8
b 81	B 51	900	600	1.2	1.0	2.5	95.3	2.3
			700	1.2	0.8	6.9	91.1	21.6
			800	1.6	1.0	6.7	90.7	26.0
			900	1.6	4.0	12.4	82.0	63.8
			1000	17.0	5.0	75.3	2.7	89.0

7. Lebensdauer und Vergiftung des Katalysators. Bestimmung der Lebensdauer, eine wichtige Eigenschaft des Katalysators, ist sehr schwer. Ich habe sie durch Gebrauch des Katalysators in Nickel-Alumina-Kaolin Reihe durch längere Zeit versucht. Die Resultate sind in Tafel 27 gezeigt. Katalysator B 58 ist unter verschiedenen Katalysatoren der wirksamste. Er wird unter Rücksicht der oben erwähnten Faktoren hergestellt und kann lange gebraucht werden.

Tafel 27.

Exp. Nr. b 52, Reak. Temp. 600°C., Kat. Nr. B 58, $H_2O/CH_4 = 10.0$, Gas. Ges. 5 lt/St.

Verlauf Stunde	CO_2	CO	H_2	CH_4	Z.G.	Volumzunahme Mal.
1	19.2	1.8	78.0	1.0	95.5	5.2
10	19.1	1.8	78.9	0.2	99.0	5.2
20	18.5	2.1	79.4	0.1	100.0	5.2
30	19.1	2.6	78.2	0.1	99.5	5.2
40	19.6	1.6	78.4	0.4	98.5	5.2
50	19.5	2.9	77.2	0.6	98.2	5.2
60	19.1	2.0	78.9	0.0	100.0	5.0
70	19.1	1.7	78.5	0.7	96.7	5.1
80	19.1	2.6	77.3	1.0	95.5	5.0
90	19.2	3.2	77.0	0.6	97.5	4.9
100	19.6	2.0	78.3	0.1	99.5	5.1
110	18.9	2.4	78.3	0.4	98.2	5.2
120	18.4	2.9	78.6	0.1	99.5	5.2
130	19.4	2.4	77.4	0.8	96.5	5.1
140	19.3	2.0	78.5	0.2	99.0	5.2
150	19.3	1.5	78.6	0.6	97.2	5.2

Die Vergiftung des Katalysators beruht hauptsächlich auf der oben erwähnten Ursache. Schwefel und Arsen unter 0.004 g. in NM Gas beeinträchtigt bei höherer Temperatur das Vermögen nicht. Der aus Nickelsulfat hergestellte Katalysator hat nachfolgendes Vermögen, wie in Tafel 28. Schwefel hat wenig Einfluss auf die Reaktionen.

Tafel 28.

Exp. Nr. f 25, Kat. Nr. F 25, Gas. Ges., 5 lt/St., $H_2O/CH_4 = 10$.

Reakt. Temp. °C.	CO_2	O_2	CO	CH_4	H_2
600	10.6	0.4	1.0	44.8	43.2
700	12.8	0.2	4.8	10.6	71.5
800	12.6	0.2	8.6	2.4	76.2
900	10.4	0.2	10.2	0.8	78.4
1000	13.0	0.2	7.8	0.0	79.0

Herstellungsweise des Katalysators ist sehr wichtig, so hat der aus Alumina und Nickelhydroxyd durch Mischung hergestellte Katalysator gutes Vermögen, aber der aus kolloidalem aktiven Alumina Gel oder Natriumaluminat Lösung mit überschüssigem Alkali hergestellte Katalysator zeigt kein Vermögen, auch wenn durch wieder holtes Auswaschen das Alakali entfernt ist.

Zwischen Silika und kolloidalem aktiven Silikagel besteht das gleiche Verhältnis. Gemisch aus Magnesia oder Kalk und Nickelhydroxyd in trockenem Zustand zeigt gutes Vermögen, aber das in feuchtem Zustand hergestellte zeigt kein Vermögen. Diese Resultate sind in Tafel 29 gezeigt.

Tafel 29.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 10$.

Exp. Nr.	Katalysator.	Reak. Temp. °C.	CO_2	CO	H_2	CH_4	Z.G.
b 95	Nickel + Magnesia (10%) F 1—F 5	600	1.2	1.2	0.0	96.4	1.2
		700	1.2	1.0	0.0	96.0	1.2
		800	1.4	1.6	2.0	93.2	3.1
		900	3.1	2.4	11.7	82.7	6.7
		1000	7.5	4.8	39.2	48.2	20.9
f 18	Nickel + Kalk F 18	590	0.0	0.0	0.0	99.8	
		680	4.4	0.0	0.0	95.4	
		800	9.8	0.4	29.6	60.0	
		890	12.7	2.0	54.8	30.5	
		1000	13.8	6.4	68 8	11.0	

Tafel 29.—(fort.)

Exp. Nr.	Katalysator.	Reak. Temp. °C.	CO_2	CO	H_2	CH_4	Z.G.
b 01	Nickel + aktiv Alumina	600	0.8	0.0	0.0	99.2	
		700	0.6	0.0	0.0	99.4	
		800	0.8	1.8	1.0	98.2	
		900	2.8	1.8	1.0	94.4	
		1000	3.3	3.0	11.0	83.6	

8. Katalysator mit Alkalizusatz. Es wird gesagt, dass Katalysator mit kleiner Menge Alkali vortreffliches Vermögen hat. Zur Feststellung habe ich folgende Experimente vorgenommen. Tafel 30 ist ein Teil der Resultate. Ich kann es nicht beweisen, bin aber der Meinung, dass der Zusatz einer kleinen Menge Allkali unter 0.01 Mol das katalytische Vermögen nicht herabdrücke. Er macht aber das Leben des Katalysators kürzer.

Diese Resultate sind in Tafel 31 gezeigt.

Tafel 30.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 10$.

Exp. Nr.	Kat. Nr.	Bestandteil Kom des Katalysators	Träger	Reak. Temp.	CO_2	CO	H_2	CH_4	Z.G.
b 4	B 3	Nickel	Feuerfester Ziegel	500	17.7	2.5	65.6	14.2	58.7
				600	17.6	2.0	70.6	9.8	66.7
				700	16.9	3.5	69.2	10.4	66.2
b 1	B 1	$Ni\text{-}K_2CO_3$		500	16.2	1.2	65.4	17.2	50.1
				600	16.1	4.4	70.0	9.5	68.2
				700	14.1	5.8	67.2	12 9	60.7
b 25	B 17	$Ni\text{-}Al_2O_3$		500	19.8	1.3	72.7	6.2	77.2
				600	18.1	2.4	74.7	4.8	81.0
b 2	B 2	$Ni\text{-}Al_2O_3\text{-}K_2CO_3$		500	18.9	3.0	71.2	6.9	76.2
				600	17.4	3.2	74.2	5 2	79.8
				700	17.0	4.3	76.7	2.0	91.4
				800	17.7	3.6	75.7	3.0	87.6
				900	16.9	4 9	75.5	2.8	88.5
				1000	14.8	7.3	75.6	2.3	90.6
b 22	B 15	$Ni\text{-}Al_2O_3$	Bimsstein	500	18.1	3.1	76.9	1.9	91.7
				600	17.9	4.0	77.1	1 0	95.4
				700	17.2	4.5	78.3	0.0	100.0
b 7	B 4	$Ni\text{-}Al_2O_3\text{-}K_2CO_3$		500	18.8	2.1	74.2	4.9	81.0
				600	18.8	2.4	77.8	1.0	95.5
				7 0	18 8	2.6	77.4	1.2	94.7
				800	18.4	3.2	77.5	0.9	96.0
				900	17.1	3.6	78.5	0.8	96.5
				1000	16.4	5.4	77.6	0.6	97.2

Tafel 31.

Exp. Nr. b 19, Kat. Nr. B 10, Gas. Ges. 5 lt/St., $H_2O/CH_4 = 7$, Reak. Temp. 600°C.

Verlauf Stunde	CO_2	CO	H_2	CH_4	Z.G.
1	17.8	4.0	77.2	1.0	95.5
5	16.9	3.6	78.5	1.0	95.4
10	17.3	3.8	78.5	0.5	97.7
20	18.0	1.8	79.4	0.8	96.0
28	16.4	4.3	78.8	0.5	97.5
30	16.9	2.2	71.4	9.5	66.7
31	11.2	2.3	42.4	44.1	23.2

(*Fortsetzung folgt*)

Naturgasforschungsinstitut des Generalgouvernements von Taiwan.

Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. IV. Analyses of the Sulphur-Containing Compounds, Coals.

By Toraki KIMOTO, Kiyoshi MORIKAWA and Ryonosuke ABE.

(Received July 4, 1941.)

The method so far developed can not successfully be applied to the sulphur-containing compounds.

Coals contain 0.3–3% of sulphur and give on heating hydrogen sulphide which poisons and reduces the activity of nickel catalyst. We have tried to fix the sulphur as copper sulphide, placing the reduced copper between the Pt-silica gel catalyst and the nickel catalyst in the reaction tube.

Experimental Details. *The apparatus* used and the procedure employed are described in the previous papers.[1][2]

The desulphuring agent. Copper oxide is easily and completely reduced by hydrogen at moderate temperature, and therefore, the unfavorable reaction of hydrogen sulphide with copper oxide is excluded.

(1) K. Morikawa, T. Kimoto and R. Abe, this Bulletin, **16** (1941) 1.
(2) K. Morikawa, T. Kimoto and R. Abe, ibid, **16** (1941) 33.

Furthermore copper combines with sulphur very tenaciously and is difficultly reduced by hydrogen under ordinary conditions. These properties of copper were thought to be very suitable for fixing sulphur from the hydrogen stream in this analytical procedure. Kieselguhr is impregnated with copper nitrate solution and the resultant dried mass was ignited.

The 15 g. of copper oxide-kieselguhr mixture thus prepared were inserted between Pt-silica gel catalyst and Ni-thoria catalyst and completely reduced in situ before the analysis.

The time required for analysis. As the amount of kieselguhr was increased the time required for analysis was prolonged to 70 minutes.

Sample:coal. Three kinds of coal of different ranks were used and their analytical data were given in Table 6.

Table 6. Ultimate analyses of sample ccals.

Kinds	Ash %	C %	H %	N %	S %	O %	O (pure coal)
Jarahinol.	4.43	67.52	4.54	1.17	0.18	22 16	23.18
Fushun	2.33	76.63	5.30	1.25	0.48	13.96	14.30
Tatong A	2 94	81.99	4.41	0 89	0 37	9.40	9.68
Tatong B	5.18	79.65	4.24	0.78	0 50	9.65	10.18
Tatong C	8.48	76.04	4.78	0 89	0 35	9.46	10.34

Experimental Results. *Examination of Absorbents.* Coals contain nitrogen and, therefore, give ammonia in the process of this analytical method. Inaba and Abe proved that coal which contained 1–2% of nitrogen gave appreciable amount of ammonia, i.e., 2.0 mg. in this procedure. They caught ammonia, by 0.02 N sulphuric acid solution and water by calcium chloride. In the experiments shown in Table 7. We found that copper catalyst not only caught sulphur and extended the life of Ni-catalyst but also decomposed ammonia to its elements and decreased partial pressure of ammonia to the negligible extent; therefore, calcium chloride could be more conveniently used than caustic soda as the absorbent for water.

Table 7. Examination of $CaCl_2$ as the absorbent for water. Analytical condition; Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hyrogen streaming velocity 5 l./hr., time for analysis 70 min., Sample; mixture of saccharose and dimethylglyoxime.

Expt. No.	Sample (g.)	N % in sample	Formed NH_3 (mg.)	O % (Found)	O % (Calculatad	Error %	absorbent
D-3	0.1510	2.23	0.30	48.78	49 15	−0.37	0.02 N H_2SO_4 + $CaCl_2$
D-6	0.2914	1.51	0.45	49.95	49.90	+0.05	
D-5	0.1907	1.47	0.30	48.94	48.83	+0.11	
D-9	0.1487	3.02	—	48.62	48.41	+0.21	$CaCl_2$
D-7	0.1897	2.12	—	49.05	49.34	−0.29	,,
D-8	0.2134	1.45	—	50.20	49.96	+0.24	,,

Effects of coal ash. We are accustomed to determine the inorganic substances in coal by burning the coal in air and weighing the calcined residue, that is, the ash of coal. It is clear that we deal not with the real inorganic substances as present in coals, but with the oxidized forms. Here on the contrary, in this procedure we are concerned with the reduced forms instead of the real inorganic substances. Considering the nature and composition of inorganic substances which occur in coals, we expect, in general, but not necessarily always, higher values of oxygen by hydrogenation than ordinary oxidation method. The results given in Table 8 may be taken as a good example.

Table 8. Results of direct determination of oxygen in the coals. Analytical condition; Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l. / hr., analytical period 70 min., absorbent: granules of caustic soda.

Expt. No.	Kind of samples	Heating temp. of the sample	Sample (g.)	Oxygen %	Difference between hydrogenation and oxidation methods.
D-32	Jarahinol	950°C.	0.2125	24.02	+0.84
D-33	,,	800	0.2050	23.62	+0.44
D-28	Fushun	950	0.2177	14.79	+0.49
D-29	,,	950	0.2508	14.86	+0.56
D-35	,,	900	0.2372	14.91	+0.61
D-39	,,	800	0.2287	14.88	+0.58
D-45	Tatong A	950	0.1934	10.22	+0.54
D-43	Tatong B	950	0.2354	10.47	+0.29
D-44	Tatong C	950	0.1999	10.77	+0.43

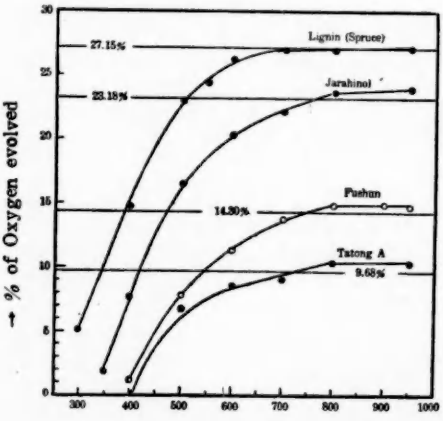


Fig. 15. Relation between the temperature of heating sample and % of oxygen evolved from the various coals.

Effects of coal ranks. The relations between the temperatures of heating samples and the amounts of oxygen caught as water were plotted in Fig. 15.

Degree of polymerisation increases in the order of lignin, Jarahinol, Fushun, and Tatong coals. Extrapolating the curves to the abscissa we know the decomposition temperature of each sample and found that the higher the polymerisation degree the higher the decomposition temperature. Above 800°C. all the three coals gave constant amounts of oxygen which were 0.5% higher than the values obtained by usual combustion method. The presence of copper

extended the life of Ni-thoria catalyst and it was actually possible to repeat the analysis 18–20 times with coal samples. Pt-silica gel catalyst was so stable that we could recover the activity by burning the free carbon deposited on the catalyst and found not necessary to replace it during year's experiments.

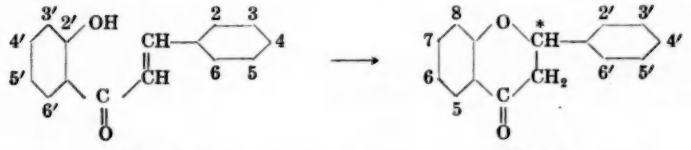
Coal Section of Fuel Department, Central Laboratory
South Manchuria Railway Co., Dairen Japan.

Asymmetrische Synthese. II. Asymmetrische Synthese von Oxy-flavanon aus Oxy-chalkon[1].

Von Haruo TATSUTA.

(Eingegangen am 18. Juli 1941.)

In einer früheren Mitteilung berichten S. Fujise und H. Sasaki[2] über die asymmetrische Synthese von *d*-Diacetyl-matteucinol (6,8-Dimethyl-5,7-diacetoxy-4′-methoxy-flavanon) aus 2′, 4′, 6′-Triacetoxy 3′, 5′-dimethyl-4-methoxy-chalkon. In der vorliegenden Mitteilung möchte ich über die Resultate der asymmetrischen Synthesen von 7-Oxyflavanon, 5,7-Dioxy-flavanon und Homoeriodictyol (5, 7, 4′-Trioxy-3′-methoxy-flavanon) aus dem entsprechenden Oxy-chalkon (bzw. Acetoxy-chalkon) berichten.



Chalkon Flavanon

* = asymmetrisches Kohlenstoffatom.

Über die Bedingungen der Umwandlung von Oxy-chalkon in optisch-aktives Oxy-flavanon spielten die Zusatzmenge der optisch-aktiven Säure (*d*-Camphersulfonsäure), die Reaktionstemperatur und die Dauer der Erhitzung eine wichtige Rolle.

Glücklicherweise ist mir die Isolierung der optisch-aktiven Oxyflavanonen aus den entsprechenden Oxy-chalkonen gelungen.

S. Fujise und A. Nagasaki[3] haben schon über die Spaltung von

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(1) Diese Mitteilung wurde schon auf Japanisch berichtet. *J. Chem. Soc. Japan*, **61** (1940), 1048.

(2) S. Fujise und H. Sasaki, *J. Chem. Soc. Japan*, **59** (1938), 440; *Ber.*, **71** (1938), 341.

(3) S. Fujise und A. Nagasaki, *J. Chem. Soc. Japan*, **57** (1936), 1245; *Ber.*, **69** (1936), 1893.

d,l-7-Oxy-flavanon in die Antipoden mittels *l*-Methoxy-acetylchlorids berichtet. Sie erhielten *d*-7-Oxy-flavanon vom Schmp. 181–182°C., $[\alpha]_D^{14} + 33.3°$. Der Drehungswert meiner Substanz ist nahezu der gleiche, daher tritt wahrscheinlich bei meinem Versuche eine fast 100%ige asymmetrische Synthese ein.

Die niedrige Drehungswert von *d*-5,7-Dioxy-flavanon und *d*-Homoeriodictyol verursacht die Mischentstehung der Racematen. Aus der Tabelle ist zu ersehen, dass die asymmetrische Synthese vielmehr von der Reaktionstemperatur und der Zeitdauer abhängig ist, als von der Menge der *d*-Camphersulfonsäure.

opt.-aktiv. Oxy-flavanone	Chalkon g.	Alkohol c.c.	*d*-Camphersulfonsäure g.	Temperatur °C.	Zeit (Stdn.)	Schmp. °C.	$[\alpha]_D$ (in Dioxan)
d-7-Oxy-flavanon	2′,4′-Dioxy-chalkon						
Nr. 1	1.0	12	0.30	115–120°	66	180–181°	$[\alpha]_D^{10}$ +29.3°
Nr. 2	1.2	14	0.30	93–100° 115–120°	48 24	187°	$[\alpha]_D^{15}$ +5.6°
Nr. 3	1.0	12	0.06	113–117°	48	186.5-187°	$[\alpha]_D^{15}$ +0.9°
d-5,7-Oxy-flavanon	2′,4′,6′-Triacetoxy-chalkon						
Nr. 1	1.0	18	0.30	115–120°	66	190°	$[\alpha]_D^{10}$ +9.8°
Nr. 2	1.0	18	0.037	112–119°	40	193.5-194°	$[\alpha]_D^{16}$ +4.4°
Nr. 3	1.2	21	0.24	98–100°	48	190°	$[\alpha]_D \fallingdotseq 0$
d-Homoeriodictyol	Acetoxy-chalkon (Schmp. 158°)[4]						
Nr. 1	0.8	32	0.05	113–117°	48	224°	$[\alpha]_D^{15}$ +8.0°
Nr. 2	0.6	24	0.12	98–100°	48	221°	$[\alpha]_D^{15}$ +6.3°

Beschreibung der Versuche. (1) *d-7-Oxy-flavanon.* 2′, 4′-Dioxy-chalkon und Alkohol wurden nach Zusatz von *d*-Camphersulfonsäure im Einschlussrohr mittels Ölbad erhitzt. Die Substanzmenge usw. wurden in der Tabelle angegeben. Die Farbe der Lösung wandelte sich von gelb zu hellrot um. Nach dem Erkalten wurde die Hauptmenge des Alkohols im Vacuum verjagt, die abgeschiedenen Krystalle wurden einmal mit wenig Alkohol und dann mehrmals mit Wasser gut gewaschen.

Die Krystalle zeigen nach dem Umlösen aus Alkohol (unter Zusatz von Entfärbungskohle) einen Schmp. von 180–181°C. (Schmp. des *dl*-7-Oxy-flavanons ist 189°C.). $[\alpha]_D^{10}$ +29.3° (in Dioxan). Gefunden: C, 74.74; H, 5.10. Berechnet für $C_{15}H_{12}O_3$: C, 75.0; H, 5.0%.

(2) *d-5, 7-Dioxy-flavanon.* 2', 4', 6'-Triacetoxy-chalkon (Schmp. 116°C.) wurde durch Acetylierung von 5, 7-Dioxy-flavanon mittels Essigsäureanhydrids und wasserfreien Natriumacetats gewonnen. Die Aufarbeitung des Reaktionsansatzes geschah wie bei (1). Nach Beendigung der Reaktion roch die Lösung stark nach Essigester. Die rohen Krystalle wurden zuerst mit wenig Petroleumäther und Alkohol, dann mit viel Wasser gut gewaschen, sie wurden aus Alkohol umkrystallisiert und schmolzen bei 190°C. (*d,l*-5, 7-Dioxy-flavanon schmolz bei 203–204°C.) $[\alpha]_D^{19}$+9.8° (in Dioxan). Gefunden: C, 70.29; H, 4.79. Berechnet für $C_{15}H_{12}O_4$: C, 70.3; H, 4.7%.

(3) *d-Homoeriodictyol.* Das Acetoxy-chalkon (Schmp. 158°C.)[4] wurde aus Homoeriodictyol dargestellt. Die Aufarbeitung geschah wie bei (1) und (2).

Die gereinigten Krystalle schmolzen bei 224°C. (Das Racemat schmolz bei 224–225°.C.). $[\alpha]_D^{16}$+8.0° (in Dioxan). Gefunden: C, 63.38; H, 4.94. Berechnet für $C_{16}H_{14}O_6$: C, 63.6; H, 4.7%.

Es sei mir erlaubt, Herrn Prof. Dr. S. Fujise für seine liebenswürdige Anleitung zu dieser Arbeit meinen herzlichen Dank auszusprechen.

Chemisches Institut, Wissenschaftl. Fakultät,
Tohoku Kaiserl. Universität, Sendai.

Synthese von rac. 3,6-Dimethoxy-5-äthoxy-*N*-äthyl-nor-aporphin[1].

Von Kakuji GOTO, Reikichi INABA und Hideo SHISHIDO.

(Eingegangen am 19. Juli 1941.)

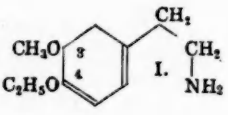
Bei der Konstitutionbestimmung von Tuduranin auf synthetischem Wege[2] haben wir auch die Gelegenheit gehabt, rac. 3,6-Dimethoxy-5-äthoxy-*N*-äthyl-nor-aporphin aufzubauen. Diese Substanz wurde zuerst zum Zwecke von Vergleich mit dem *N*-Aethyl-tuduranin-äthyl-äther synthetisiert, aber bei ihrem Abbau zu Vinyl-phenanthren ergab sich, dass sie nur eine isomere Substanz darstellt. Da der Gang der Synthese ganz

(4) Der Verf. benutzte etwas unreinen Krystall.
Die reinste Krystalle schmolzen bei 163-164°C., vgl. Shinoda und Sato, *J. Pharm. Soc. Japan*, **49** (1929), 64.

(1) 49. Mitteilung über Sinomenin.

(2) K. Goto und H. Shishido, *Ann.*, **539** (1939), 262; Goto u.a., *Ann.*, **530** (1937), 142.

gleich mit demjenigen des rac. *N*-Aethyl-tuduranin-äthyl-äthers ist, möchten wir ihn nur schematisch unten abbilden und die Beschreibung der einzelnen Substanzen sollen möglichst kurz angegeben werden.



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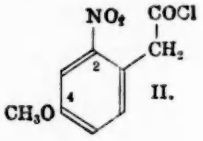

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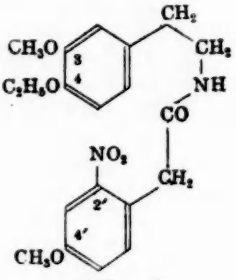

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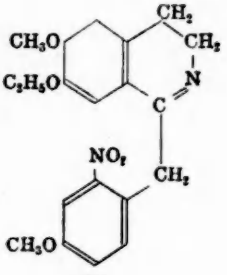

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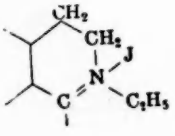

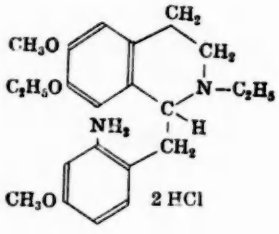

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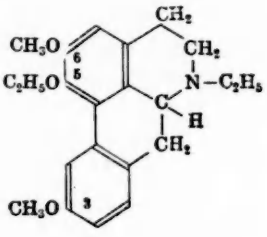

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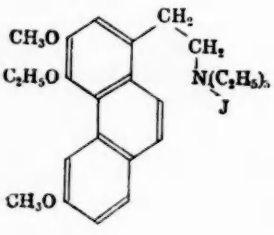

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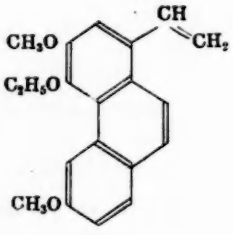

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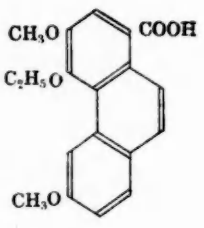

IX.

Versuche. *β - (3 - Methoxy-4-äthoxy-phenyl)-äthyl-2'-nitro-4'-methoxy-phenacetamid* (III). Aus 3 - Methoxy-4-äthoxy-phenyl - äthyl-amin (I)[3] und 2-Nitro-4-methoxy-phenyl-essigsäure-chlorid (II)[4]. Weisse,

(3) Die hierzu nötige 4-Aethoxy-3-methoxy-phenylessigsäure wurde durch Kondensation von Aethyl-vanillin mit Essigsäure und darauffolgende Reduktion dargestellt. Die Säure wurde zuerst ins Chlorid und dann Amid nach Perkin (*J. Chem. Soc.*, **125**, 1679.) umgewandelt, daraus das Amin (I) durch NaOCl bereitet wurde.

(4) *J. Chem. Soc.*, **119**, 1630; *Helv. Chim. Acta*, **15** (1932), 398.

haarige Nadeln aus Methanol. Schmp. 132°C. Gefunden: C, 61.56; H, 6.08. Berechnet für $C_{20}H_{29}N_2O_6$ (388): C, 61.86; H, 6.19%.

2'-Nitro-4'-methoxy-1-benzyl-β-(6-methoxy-7-äthoxy)-3, 4-dihydro-isochinolin (IV). Bereitet durch die Einwirkung von P_2O_5 auf dem Phenacetamid (III) in getrocknetem Toluol bei der Siedehitze. Das Dihydro-isochinolin wurde aus verdünnter salzsaurer Lösung mit Alkali befreit und durch Aether aufgenommen. Der Aether-rückstand wurde aus Methanol umkrystallisiert. Prismen. Schmp. 139–141°C. (verschwärzt; sintern ab 134°C.). Gefunden: C, 64.96; H, 6.07. Berechnet für $C_{20}H_{22}N_2O_5$ (370): C, 64.86; H, 5.95%.

Jodäthylat. Durch Erhitzen der freien Base bei 100°C. mit überschussigem Aethyljodid im Druckflasche. Gelbe Prismen aus 95 proc. Aethanol. Schmp. 206–207°C. (zers.). Gefunden: C, 50.05; H, 5.26. Berechnet für $C_{22}H_{27}N_2O_5J$ (526): C, 50.19; H, 5.13%.

2'-Amino-4'-methoxy-β-(6-methoxy-7-äthoxy)-1-benzyl-2-äthyl-tetrahydro-isochinolin-dichlorhydrat (V). Das obige Jodäthylat wurde in konz. Salzsäure mit Zinkpulver reduciert. Nach Filtrieren und Alkalisieren wurde das entstandene Tetrahydro-isochinolin in Aether aufgenommen. Das Dichlorhydrat krystallisierte beim Zusatz von wenig 10 proc. Salzsäure zum Aether-rückstand. Weisse Prismen aus Wasser. Schmp. 185–188°C. (zers.; sintern ab 178°C.). Gefunden: C, 57.94; H, 7.47. Berechnet für $C_{22}H_{32}N_2O_3Cl_2+\frac{1}{2}H_2O$ (452): C, 58.41; H, 7.30%.

Racem. *3, 6-Dimethoxy-5-äthoxy-N-äthyl-nor-aporphin* (VI+ HCl). Das Dichlorhydrat (V) wurde in Methanol gelöst und mit 2 N Schwefelsäure und berechneter Menge $NaNO_2$ diazotiert. Nach dem Zersetzen der Diazonium-gruppe durch Erhitzen bei 100°C., wurde die Lösung mit Salzsäure und Zinkpulver entfärbt. Die mit Aether gewaschene Lösung wurde alkalisiert und mit Aether extrahiert. Durch Versetzen mit Salzsäure zum Äther-rückstand das racem. Aporphin als Chlorhydrat isoliert. Prismen aus Wasser. Schmp. 256–262°C. (zers.). Gefunden: C, 67.41; H, 7.35. Berechnet für $C_{22}H_{27}NO_3 \cdot HCl$ (389,5): C, 67.78; H, 7.19%.

Die racem. freie Base (VI) krystallisiert aus Aether in grossen Tafeln. Schmp. 105–107°C. Gefunden: C, 74.77; H, 7.64; N, 4.06. Berechnet für $C_{22}H_{27}NO_3$ (353): C, 74.79; H, 7.65; N, 3.97%.

Des-N-diäthyl-3,6-dimethoxy-5-äthoxy-nor-aporphin-jodäthylat (VII). Das Jodäthylat (Schmp. 184–186°C. (zers)) vom obigen Aporphin (VI) wurde durch Kochen mit 11% NaOH in die des-*N*-Diäthyl-base umgewandelt. Da die letztere keine Neigung zur Krystallisation zeigte, wurde sie als Jodäthylat (Schmp. 160–164°C.) analysiert. Gefunden: C, 56.96; H, 6.82; N, 2.20. Berechnet für $C_{26}H_{36}NO_3J+\frac{1}{2}H_2O$ (546): C, 57.14; H, 6.78; N, 2.56%.

3,6-Dimethoxy-5-äthoxy-8-vinyl-phenanthren (VIII). Das oben genannte Jodäthylat (VII) wurde durch Kochen mit methanolischem Natron desaminiert. Der Vinyl-Körper wurde mit Aether gesammelt und aus Aethanol umkrystallisiert. Prismen. Schmp. 79–81°C.[5] Gefunden: C, 77.48; H, 6.44. Berechnet für $C_{20}H_{20}O_3$ (308): C, 77.92; H, 6.49%.

(5) Das Dimethoxy-äthoxy-vinyl-phenanthren aus Tuduranin schmilzt bei 108°C. (loc. cit., S. 263 Anm.)

Die Vinyl-seitenkette wurde durch Oxydation mit Kalium-permanganat in Aceton (bei 40–45°C.) ins Carboxyl verwandelt. Die 3,6-Dimethoxy-5-äthoxy-phenanthren-carbonsäure (IX) krystallisierte in Prismen und schmolz bei 185–187.5°C., also um etwa 7°C. höher als die 3-Aethoxy-5,6-dimethoxy-phenanthren-8-carbonsäure, bereitet aus Tuduranin.

Alle Analysen wurden von Firma Takeda in Osaka ausgeführt, dafür sprechen wir unseren besten Dank aus.

An Electron Diffraction Study of the Protective Coating on Metals and Alloys (*Continued*): the Acid-Proof Surface of Ferrosilicon (Duriron).

By Shigeto YAMAGUCHI.

(Received June 27, 1941.)

Introduction. It is well-known that an alloy[1] of Fe and Si containing about 14% Si is one of the few alloys capable of resisting the corrosive action of sulphuric acid, but the state of this acid-proof surface as well as the surface substance produced here inhibiting the corrosive action of the acid have escaped study, because it is very difficult to detect such thin films by the usual methods except the electron diffraction method. The present study by the latter method can successfully produce the entity of the protective coating obtained over the silicon-iron alloy immersed in sulphuric acid solutions.

When aluminium bronze was heated in the air, electron diffraction analyses only γ-Al_2O_3 over the surfaces of these alloys.[2] The mechanism of this "selective oxidation" is at present being discussed by many investigators throughout the world, but no interpretation regarding this phenomenon can be held as conclusive.[3][4][5] A selective oxidation by sulphuric acid solution, not by air, was found through the present study, and consequently this phenomenon can be considered from a point of view other than those assumed by the above investigators.

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(1) Woldman and Dornblatt, "Engineering alloys." 1936.
(2) I. Iitaka and S. Miyake, *Nature*, **136** (1935), 437; **137** (1936), 457.
(3) G. D. Preston and L. L. Bircumshaw. *Phil. Mag.*, **20** (1935), 706.
(4) S. Dobinski, *Nature*, **141** (1938), 81; **144** (1939), 510.
(5) H. Bienfait, *Nature*, **145** (1940), 190.

Electron Diffraction Experiments. A piece of ferrosilicon ("Duriron") (Si: ca. 15%), whose macro-structure as seen through the microscope consists mainly of Fe-Si solid solution intermixed with a small quantity of Fe_2Si_3, was adopted as a specimen. The corrosive reagent was sulphuric acid at various concentrations (5~20 N); the experimental results obtained were always the same.

Experiment 1. On immersing the specimen in the sulphuric acid solution, a faint generation of gas bubbles (H_2) was observed for 5~10 minutes, and then this phenomenon ceased. The surface of the specimen in this state has a gray colour and possesses a practically perfect acid-proof nature. An electron diffraction analysis was made on this surface. The four spacings corresponding to the four weak rings observed in the diffraction pattern here obtained were determined by repeating the experiment about twenty times.* However, since it was difficult to determine the entity of the substance giving these four rings on the basis of these four spacings alone, further experiment was carried out.

Table

d	d_{obs}	$d_{x\text{-ray}}$	h k l	I_{obs}
—	—	4.90	1 1 0	—
3.60	3.60	3.58	2 0 0	m
—	3.00	2.99	2 1 1	s
2.15	2.16	2.20	3 1 0	s
1.84	1.84	1.87	3 2 1	s
—	1.53	1.56	4 2 0	f
1.35	1.36	1.37	4 3 1	s
—	1.26	1.28	5 2 1	s
—	1.08	1.13	5 3 2	f

d: Spacings characteristic of the surface of the sample.
d_{obs}: Spacings of α-cristobalite crystal.
$d_{x\text{-ray}}$: Spacings of α-cristobalite observed by x-ray.
h k i: Miller Indices.
I_{obs}: Intensity of the rings observed here.

Experiment 2. As may be suggested in Experiment 1, the crystals producing the above four spacings must be a weak electron scatterer, i.e., the existence of silica (SiO_2) on the acid-resisting surface of Duriron is suspected. According to our physical and chemical studies the following modifications of SiO_2 are known:

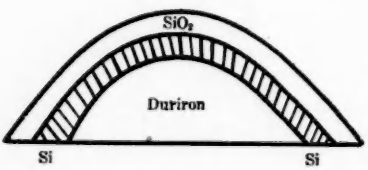
* It was vain to expect that the diffraction rings from α-Fe (body-centred structure) will be observed here. This fact suggests the formation of some protective coating over the specimen, since a heavy metal Fe diffracts intense electron beam.

α- and β-Cristobalite
α- and β-Tridymite
α- and β-Quartz.

Of these six modifications the existence of α-cristobalite is not only the most probable, but also it is the form appearing at low (room) temperature.[6] The present author carried out an experiment here: pure α-cristobalite was chemically prepared and the diffraction pattern, consisting of many obvious rings, from α-cristobalite was directly compared with that from the surface of Duriron passive to sulphuric acid.

The thin film of α-cristobalite for the experiment was produced by making beforehand a film of water-glass over a platinum wire-gauze and then by dropping hydrochloric acid upon it.* The values of spacings determined with the rings from pure α-cristobalite were, as listed in the table, in accordance with those of α-cristobalite by X-ray study. As may be seen in the table, the values of d agree with those of d_{obs} satisfactorily, and therefore there is no room for doubt that the acid-proof surface of ferrosilicon (Duriron) is coated with small crystals of α-cristobalite.

Discussion. Under the same conditions, not only Fe but also Si in the solid solution of the iron silicon alloy must be attacked by the corrosive molecule or ion; but the reaction product of the former is easily soluble in water,** whereas that from the latter is insoluble in water. It is chemically well-known that pure silicon is practically unattacked by common mineral acids (HCl, H_2SO_4, HNO_3, etc.). However, the present study concludes that the silicon surface immersed in acid is coated with SiO_2 (α-cristobalite) small crystals. Since the surface or the superficial layer of Duriron immersed in acid is α-cristobalite small crystals, the second layer lying below the SiO_2 layer should be chiefly silicon or the silicon-rich layer, and below this layer lies the alloy substrate. A picture of the condition of the layers imparting the acid resistant property is shown in the figure.



The iron in the alloy is coated with Si and SiO_2 which are both resistant toward acid; as it were, "a protective double layer" exists on the iron alloy. It is due to this double layer that the iron silicon alloy is able to resist satisfactorily the attack of sulphuric acid.

(6) T. F. W. Barth, *Am. J. Sci.*, **23** (1932), 350; **24** (1932), 97.

* The platinum wire-gauze used here has been explained many times in my previous papers; e.g., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*.

The NaCl solution produced over the wire-gauze was removed with a small piece of clean filter paper.

** Fe in the solid solution exists in the same state as in metallic iron, because the ferrosilicon used here contains no compound between Fe and Si.

As a matter of fact, the corrosive solution (sulphuric acid) altered the colour of ferricyanide solution to blue.

When Fe in the solid solution is removed by the acid and Si remains adhering to the metal substrate, many small protuberances consisting of Si posessing free bond are produced on the surface of this alloy. This silicon atom has a large chemical affinity and can give SiO_2 more easily than ordinary silicon. Although the gaps are partly packed with SiO_2 crystals, the recrystallization of the active silicon, i.e., the metallic bond formation of Si helps partly the packing of the gaps.

The phenomenon of formation of SiO_2 over the ferrosilicon is doubtlessly selective oxidation of the alloy taking place in solution. The "selective oxidation" which has been often discussed only with the oxide obtained in air can here be considered from another point of view.

The selective oxidation of Duriron by sulphuric acid is realized as a result of the following chemical and physical processes:

(1) Fe, a component weak towards acid is removed from the metal surface,

(2) Si, a component strong towards acid remains over the metal surface, becoming a protective coating of SiO_2, and recrystallization of Si and SiO_2 occurs in order to stretch over the surface and covering the metal substrate. If the analogy between this selective oxidation in solution and that in air is permitted, in the latter environment also the processes (1) and (2) should take place. When on the surface of aluminium bronze oxidation by air takes place, process (1) results in that the CuO produced on the surface exfoliates, because it is produced comparatively coarse and does not adhere strongly to the metals substrate, while the γ-Al_2O_3 produced over the alloy adheres strongly to the ground metal, for both of these oxide coatings are very thin, compact and strong as were verified in the previous study of the present author.[7]

In conclusion, I wish to express my deep thanks to Dr. Ichiro Iitaka, under whose direction this work has been undertaken, for his many important suggestions, to Prof. S. Mizushima for his sincere interest. I also take this opportunity in thanking the Nippon Gakuzyutsu Shinkokwai for the financial grant through the auspices of its Corrosion Committee.

The Institute of Physical and Chemical Research, Tokyo.

(7) S. Yamaguchi: *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **36** (1939), 463; I. Iitaka and S. Yamaguchi: *Nature*, **144**, (1939), 1090.

Researches on Camphor, Borneol and Their Allied Substances (*Continued and Concluded*).

By Seichi YAMADA.

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V. The Dehydration of Borneol and Isoborneol. (1) *The dehydration of borneol and isoborneol with* $H_2SO_4.3H_2O$. Borneol (m.p. 205°C., $[\alpha]_D$+18.62) and isoborneol (m.p. 209–210°C. in a sealed tube $[\alpha]_D$ −15.72) 10 g. of each was taken in a distilling flask, to which 0.4 c.c. of $H_2SO_4.3H_2O$ (in volume 4%) was added; and being heated at 140–145°C. for a definite time the water formed by the reaction accompanying a small quantity of camphene was distilled out. The reaction product was put into some water to be extracted with ether; and the ether solution was washed with a dilute solution of sodium carbonate and was dried to distil off the ether, and then it was fractionally distilled.

No.	Sample	Heat. hours	Yield %	Main fraction (camphene)				Fraction of higher boiling point			
				Yield %	B.p. °C.	M.p. °C.	$[\alpha]_D$	Yield %	B.p.	d_4^{20}	n_D^{20}
1	borneol	5	90	62	155–161	42–45	+3 3	13	150–167[10 mm]		
2	,,	10	93	63	155–166	43–45	+1.8	12	147–173[11] ,,		
3	,,	15	87	58	155–161	42–44	0	10	148–168[11] ,,		
4	iso-borneol	2	95	47	152–160	48–52	+4.4	20	120–147[5] ,,		
5	,,	10	89	56	154–163	47–48	+0.5	18	120–153[5] ,,	0.955	1.493
6	,,	15	91	50	152–161	42–45	0	11	120–148[5] ,,	0.956	1.493

The mixture of fractions (1), (2), (3) of higher boiling points was fractionally distilled, and a colourless viscous compound to be considered as di-*d*-bornyl ether was obtained:—

B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D^{27°}$ (in alcohol)	M.R. obs.	M.R. calc. for $C_{20}H_{34}O$
134–137[2 mm]	0.9564	1.4927	+41.68	88.15	87.40

Found: C, 82.93, H, 11.73. Calculated for $C_{20}H_{34}O$: C, 82.67; H, 11.81%.

This fraction was treated with hydrogen iodide (b.p. 125–127°C.) at 130°C. for an hour; and from the reaction product, crystal of borneol (its phenylurethane m.p. 135–137°C.) was obtained.

On the other hand, this fraction manifested no colour reaction when conc. nitric acid was added to it; and when it was heated, a yellow precipitation of camphor-like odour issued.

Next, fractions (4), (5), (6) of higher boiling points were collected

and fractionally distilled, and compounds to be considered as di-*d,l*-isobornylether were obtained:—

B.p.	d_4^{20}	n_D^{20}	M.R.
136—145$^{2.5\,mm}$	0.9672	1.5010	90.29

Found: C, 82.22, H, 11.37. Calculated for $C_{20}H_{34}O$: C, 82.67, H, 11.81%.

By treating this with hydrogen iodide, alcohol was obtained, from which phenylurethane (m.p. 139–139.5°C.) was obtained.

By treating with conc. nitric acid, it changed to a green colour, which grew reddish brown when heated. Again, when it was diluted, a yellow precipitation of camphor-like odour was obtained.

(2) *The Dehydration of Borneol with Alumina.* Borneol (m.p. 205°C., $[\alpha]_D$+18.62) was passed over alumina (Merk) heated at 350°C. at the rate of about 5 g. per hour; and the reaction product, accompanying a trace of water, was fractionally distilled. The result was as follows:—

Fraction	B.p. °C.	Yield (g.)	d_4^2	n_D	M.R.	$[\alpha]_D^{12}$ in alcohol
1	33—100	2.4	—	—	—	—
2	100—145	7.1	0.8356^{20}	1.4690^{20}	45.37	0
3	145—155	38.8	0.8312^{40}	1.4596^{40}	44.82	+0.23
4	155—155.5	36.6	0.8286^{40}	1.4627^{40}	45.22	+0.58
5	155.5—161	6.4	0.8459^{20}	1.4730^{20}	45.14	+2.31
6	161—	5.5	—	—	—	—

From the main fractions (3) and (4), solid camphene (m.p. 52–53°C., $[\alpha]_D$+0) was obtained.

(3) *The action of* $H_2SO_4.3H_2O$ *on bornyl acetate.* When borneol (m.p. 204°C., $[\alpha]_D$+38.44) was heated with glacial acetic acid and potassium acetate, the following acetic ester[38] was obtained:

B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D^{11}$
98$^{11\,mm}$	0.9864	1.4655	+42.75

To 20 g. of this ester, 0.8 c.c. of $H_2SO_4.3H_2O$ was added; and, after a reaction of 10 hours at 140–145°C., the reaction product was fractionally distilled to separate it into camphene and the ester as completely as possible:

Fraction	B.p.	Yield %	d_4^{20}	n_D^{20}	$[\alpha]_D^{12}$ in alcohol
1	30 - 82$^{5\,mm}$	8.8	0.9511	1.4727	—
2	82—84	77.0	0.9813	1.4657	+39.13
3	residue	12.1	—	—	—

(38) Bertram, *Ann.*, **231**, 304.

Of the reaction products, to the estimation of camphene, the bromine absorption was adopted, and to that of borneol and isoborneol, the phthalic anhydride method; and it was found that the reaction products were 96.5 moles% bornylester, 0.5 mole% isobornylester, and 3 moles% camphene.

(4) *Conversion of isobornylacetate to camphene by the action of* $H_2SO_4 \cdot 3H_2O$. Inactive isobornylacetate (b.p. 79.5–81.5$^{3.5mm}$, d_4^{20} 0.9848, n_D^{20} 1.4640, saponification value (obs.) 285.8, (calc.) 286) was reacted with $H_2SO_4 \cdot 3H_2O$. From the saponification value 103.2 of the reaction product, it was calculated out that the proportions of the ester and camphene were 22 moles% and 78 moles%.

(5) *The Conversion of camphene to isoborneol by the action of* $H_2SO_4 \cdot 3H_2O$. Camphene (5 g.) was dissolved in glacial acetic acid (2.5 g.), and the solution was treated with $H_2SO_4.3H_2O$ (0.2 c.c.). From the saponification value 168.2 of the reaction product, the proportions of isobornylester and camphene were calculated out to be 50 moles% and 50 moles%.

(6) *The dehydration of isoborneol with phthalic anhydride.* Isoborneol (m.p. 209–210°C., in a sealed tube, $[\alpha]_D^{18}$–15.72 in alcohol) 20 g. and phthalic anhydride (2 moles) were reacted under the following conditions:

No.	React. temp. °C.	React. hours h	Reaction product		Camphene obtained from the dehydrated oil		
			Ester (g.)	Dehydrated oil (g.)	B.p. °C.	M.p. °C.	$[\alpha]_D$
1	140–145	11	19	6.5	153–163	48–52	+ 1.34^{13}
2	110–115	13	29.5	3.5	150–157	45–47	+25.25^{14}
3	80–85	46	35.2	1.3			

The ester No. 1 was separated into 10 g. of acid ester (m.p. 164°C., $[\alpha]_D^{25}$ +43.10, C=0.99 in alcohol), 10 g. of borneol and 6.3 g. of neutral ester (m.p. 100–101°C., $[\alpha]_D^{24}$ + 27.93 C = 0.806 in alcohol). By the saponification of the ester, borneol (m.p. 205–206°C) was isolated; and when the mixture of it and other borneol was put to a mixed fusion, no depression of the melting point was seen. The ester No. 2 was separated into 10 g. of acid ester (m.p. 152°C., $[\alpha]_D$–20) and 3 g. of neutral ester (m.p. 92°C., $[\alpha]_D$–22). These esters were saponified, and isoborneol of m.p. 207°C., in a sealed tube and $[\alpha]_D$–2 was obtained from the former ester, and isoborneol of m.p. 203°C. in a sealed tube and $[\alpha]_D$–7 from the latter. Moreover, to isoborneol (m.p. 212–213°C. in a sealed tube $[\alpha]_D$–34.42) 2 moles of phthalic anhydride was added; and after a reaction at 110–115°C., camphene $[\alpha]_D^{1.5}$+49.33) was obtained.

(7) *Hydration of camphene.* From bornyl chloride (m.p. 131°C., $[\alpha]_D$ +31.29), by means of the following method, diverse camphenes were obtained.

(i) By the reaction of aniline[39] for over 10 hours, the camphene produced was of m.p. 49–52°C. and $[\alpha]_D^{19}$ 0.

(ii) Yellow lead oxide[40] was heated at about 250°C., and bornyl chloride was acted on it. The camphene thus produced was of m.p. 49.5°C. and $[\alpha]_D^{19}$ +12.86.

(iii) Camphene produced by the reaction of phenol[41] was of m.p. 48–50°C. and $[\alpha]_D^{18.5}$ + 72.69.

The specific rotation of the isoborneols obtained by the hydration of the 3 kinds of camphenes shown above is as follows:

(i) The isoborneol obtained from the camphene $[\alpha]_D^{19}$ 0: m.p. 209 (in a sealed tube), $[\alpha]_D^{19}$ 0.

(ii) The isoborneol obtained from the camphene $[\alpha]_D^{19}$ +12.86: m.p. 210°C. (in a sealed tube): $[\alpha]_D^{19}$ − 0.54.

(iii) The isoborneol obtained from the camphene $[\alpha]_D^{18.5}$ +72.69: m.p. 208°C. (in a sealed tube), $[\alpha]_D^{19}$ −5.13.

The content of borneol in the isoborneol, obtained as above, estimated by means of the phthalic anhydride method, was 10%.

Further, the influence of the time to the hydration of camphene [α] + 72.69 was investigated to be as follows:

No.	React. hours	Isoborneol ester				Isoborneol	
		B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D$ °C.	M.p.* °C.	$[\alpha]_D$ in alc. °C.
1	1/3	74—77[3.5 mm]	—	—	−11.47[20]	207—208	−10.56[19]
2	4 1/3	86[7]	0.9825	1.4656	− 7.83[9]	208.3	− 5.13[9]
3	27 1/2	88[6]	0.9825	1.4652	− 4.14[9]	—	—
4	118	85[4]	0.9813	1.4650	− 0.78[9]	206	± 0[9]

* Measured in a sealed tube.

From No. 1 unreacted camphene (m.p. 51–53°C., $[\alpha]_D^{22}$ +14.01 was separated.

(i) By the reaction between bornyl chloride and phenol, a camphene $[\alpha]_D$+72.69 was obtained, which was colourless even after hydration, and there was no change of colouration.

(ii) By the reaction between bornyl chloride and yellow lead oxide or aniline, a camphene [α] +12.86 was obtained, which became yellow when hydrated.

(iii) By the dehydration of borneol with alumina, a camphene $[\alpha]_D$0 was obtained, which, when hydrated, became faintly brown at first and changed to blackish green afterwards. Further, it became crimson red when thrown into water. This colour reaction is a phenomenon also seen in the case of hydrocarbons formed when dimethylborneol is dehydrated with $H_2SO_4 \cdot 3H_2O$.

(39) Ullmann and Schmidt, *Ber.*, **43** (1910), 3202.
(40) Tetsusaku Ikeda, *Proc. Sci. Inst.* Japan, **4** (1925), 503.
(41) A. Reychler, *Ber.*, **29** (1896), 696.

(iv) When borneol is dehydrated with $H_2SO_4.3H_2O$, a camphene $[\alpha]_D 0$ is obtained, which, in the course of hydration, becomes to a faint purple red colour at first and then changes to a faint reddish brown colour afterwards. When thrown into water, it becomes to a faint yellowish brown colour. As has been described above, according as the preparation differs, camphenes behave differently in the colour reaction by hydration. This is to be considered due to the accompanying impurities.

(8) *Racemisation of camphene by* $H_2SO_4 \cdot 3H_2O$. By the reaction between bornyl chloride and yellow lead oxide, a camphene (m.p. 52.2–52.9°C. $[\alpha]_D^{20}+8.28$) was obtained, to 10 g. of which, 0.4 c.c. of $H_2SO_4.3H_2O$ (0.05 mol) was added and it was heated at 140–145°C. Afterwards the camphene was collected and its rotatory power was examined.

No.	React. hours h	Reacv. product			Camphene			Oily part			
		B.p. °C.	Yield %	$[\alpha]_D$ °C.	M.p. °C.	Yield %	$[\alpha]_D$	Yield %	d_4^{25}	n_D^{25}	$[\alpha]_D$
1	12	154–158	72	—	52–52.4	58	0	14	0.843	1.470	+0.6
2	1	153–158	72	$+1.76^{23}$	53–54	25	+0.3	23	0.853	1.469	+1.6
3	1/6	153–155	71	+5.8	53–54	51	+5.2	2	—	1.470	—

To investigate the influence upon the racemisation of camphene at the temperature of 10–20°C., 13 g. (2.3 moles) $H_2SO_4.3H_2O$ was added to 5 g. camphene, and, after an elapse of 400 hours, it was recognised that racemisation had occurred.

No.	React. hours	React. product		Camphene	
		B.p. °C.	Yield %	M.p. °C.	$[\alpha]_D$
1	20	154—157	50	52—54	+4.8
2	412	155—170	40	48—50	+1.6

(9) *The racemisation of camphene with 50% sulphuric acid.* 5 g. camphene was treated with 0.5 g. of 50% (0.05 moles) sulphuric acid at 50–60°C.

No.	React. hours	Reaction product		Camphene	
		B.p. °C.	Yield %	M.p. °C.	$[\alpha]_D$
1	3	153—155	98	49—50	+5.2
2	24	155—159	80	52	+3.8

(10) *The recemisation of camphene with hydrochloric acid.* 10 g. camphene was treated with 0.4 c.c. $HCl \cdot 3H_2O$ at 140–145°C. Although the rate of reaction was rather slow, it was found that racemisation had occurred to some extent.

No.	React. hours	Reaction product		Camphene	
		B.p. °C.	Yield %	M.p. °C.	$[\alpha]_D$
1	1	155–162	58	51–53	+8.5
2	12	155–162	70	48–53	+5.4

(11) *The racemisation of camphene with acetic acid.* 5 g. camphene was treated with 12.5 g. (5 moles) glacial acetic acid at 50–60°C., and some evidence of racemisation was recognised.

No.	React. hours	Reaction product		Camphene	
		B.p. °C.	Yield %	M.p. °C.	$[\alpha]_D$
1	3	155–156	50	49–53	+6.2
2	12	155–156	60	49–53	+6.0

(12) *The racemisation of camphene with phthalic anhydride.* To 10 g. camphene (m.p. 47–50°C., $[\alpha]_D^{13.5}$ +49.33), a well dried 19 g. (2 moles) phthalic anhydride was added, and the mixture was heated at 140–145°C. for 11 hours. To separate out camphene from the reaction product, the extraction by petroleum ether was adopted instead of steam distillation, and the yield of camphene (b.p. 153–160°C., m.p. 46.5–47.5°C., $[\alpha]_D^{22}$ +1.9) was 50%. Although great precautions were taken not to admit the entrance of any drop of water during the reaction, there was seen at the end of the reaction neutral and acid esters of isoborneol, both insoluble in petroleum ether. When the neutral ester $C_{28}H_{34}O_4$ was recrystallised from its solution in methyl alcohol, the following substance was obtained: Neutral ester, m.p. 99–100.5°C., $[\alpha]_D^{27}$ −3.32 (C=1.8 in alcohol). Found: C, 76.65; H, 8.62. Calculated for $C_{28}H_{38}O_4$: C, 76.66; H, 8.73%.

When the acid ester $C_{18}H_{22}O_4$ was recrystallised from its solution in methyl alcohol, the following substance was obtained: Acid ester, m.p. 169–170.5°C., $[\alpha]_D^{25}$ −1.57 (C=1.91 in alcohol). Found: C, 71.47; H, 7.66; Calculated for $C_{18}H_{22}O_4$: C, 71.48; H, 7.34%.

(13) *The racemisation of camphene with alumina.* 12 g. camphene (m.p. 42–45°C., $[\alpha]_D^{18}$ +9.28) together with a small quantity of steam was passed over alumina heated to 350°C. for 7 hours, and 49% camphene (b.p. 145–156°C., m.p. 46–51°C., $[\alpha]_D^{18}$ +1.8) was obtained.

(14) *The racemisation of camphene by the application of heat.* The above camphene was passed alone through a glass tube heated to 350°C., and the camphene thus obtained was of b.p. 154–158.5°C., m.p. 45.5–46.5°C., $[\alpha]_D^{16}$ + 9.9. Therefore, no change was seen.

(15) *The racemisation of isobornyl acetate by the Bertram Walbaum's method of hydration.* The writer, dissolving camphene $[\alpha]_D^{13.5}$ +64.40 in

absolute alcohol after Kachler and Spitzer's method[42] and passing hydrogen chloride through the solution cooled with ice, obtained isobornyl chloride (m.p. 146–148°C., $[\alpha]_D^{85}$ −27.08 (C=3.46 in alcohol) in yield of 85%. It was heated to 70°C. with silver acetate in a sealed tube and there was obtained, in addition to a great quantity of camphene ($[\alpha]$+58.29), an extremely small quantity of ester ($[\alpha]_D^8$−5.71). On the other hand, isoborneol (m.p. 212–213°C., in a sealed tube) was treated both with acetic anhydride and potassium acetate for indefinite hours, and the following ester of isoborneol was obtained:

No.	React. hours	Ester of isoborneol				
		Yield (g.)	B.p.	$[\alpha]_D$	d_D^{20}	n_D^{20}
1	3	11	97–99[11 mm]	−46.73[18] C = 4.46 in alcohol	0.9882	1.4649
2	2	11	80–82[4]	−50.29[18] C = 4.23 ,,	0.9867	1.4659
3	1	10.5	76–77[3]	−51.98[18] C = 5.05 ,,	0.9867	1.4623

By saponifying the esters 2 and 3, isoborneols $[\alpha]_D$−33.18 and $[\alpha]_D$ −34.10 were obtained respectively.

To isobornyl acetate (b.p. 76–77°C.[3mm], d_4^{20} 0,9876, n_D^{20} 1.4649, $[\alpha]_D^{20}$ −47.81), each of the 50% sulphuric acid, acetic acid, and the mixture of the two was added separately, and the reaction was excited at 50–60°C. As to the specific rotation of the ester, there was no change whatever in the former two cases, while a decrement was observed in the case of the acid mixture, the detail being as follows:

No.	Sample (g.)	Catalyser (g.)	React. hours	Reaction product				
				Yield (g.)	d_4^{20}	n_4^{20}	$[\alpha]_D^{23}$	Br_2 test
1	4	acetic acid 10	3	4	0.9884	1.4644	−47.80	−
2	4	50% H_2SO_4 0.4	3	4	0.9340	1.4644	−47.51	−
3	4	acetic acid 10 50% H_2SO_4 0.4	1/3	4	0.9833	1.4649	−45.62	+
4	15	acetic acid 33 50% H_2SO_4 1.5	4	15	0.9813	1.4631	−17.08	+

No.	Isobornyl acetate				
	Yield (g.)	B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D$
1	3.5	71–72[2.5mm]	0.9856	1.4648	−47.89
2	3.2	70–71[2.5]	0.9856	1.4648	−47.43
3	3.2	71–73[2.5]	0.9852	1.4648	−45.58
4	11.5	115–116[3]	0.9813	1.4651	−19.01

(42) *Ann.*, **200**, 345.

Of the reaction products of sample No. 4, camphene was estimated by the bromine absorption to be 1.3%.

Accordingly, the reaction products were distilled, and, using the earlier distillate after Balbiano's method,[43] formed a needle-shaped addition product (m.p. 185.5–186°C.) composed of mercuric acetate and camphene, and thus the presence of camphene was confirmed. When the reaction product was once more distilled after the elapse of a whole day, a distillate b.p. 80–91°C.^{3mm}, d_4^{20} 0.9832, n_D^{20} 1.4653 was obtained; while when the distillation was tried after the elapse of 20 days, the distillate was of b.p. 81–83.5°C.$^{3.5mm}$, d_4^{20} 0.9863, n_D^{20} 1.4651. Thus an extraordinary variation[44] in the boiling point was shown. The ester, which was distilled out in the rear, was saponified; and it was found that the isoborneol thus obtained had the following properties and had accompanied neither camphenehydrate nor camphene and others.

M.p.	$[\alpha]_D^{25}$ in alcohol	$[\alpha]_D^{25}$ in toluene	M.p. of *p*-Nitrobenzoate	Methoxy value of what was methylated with HCl and CH_3OH
211–212°C. (in a sealed tube)	−16.74	−8.79	129C.°	10.9

No trace of water was generated even when isoborneol was heated to 220°C. for half an hour, and no decolourisation of bromine water was observed.

VI. The Dehydration of Dimethylborneol. (1) *The dehydration of dimethylborneol with* $H_2SO_4 \cdot 3H_2O$. Dimethylcamphor was reduced with metallic sodium and alcohol and then treated with phthalic anhydride at 110–115°C. To 50 g. of the dimethylborneol (m.p. 45–50.8°C., $[\alpha]_D^{26}$ + 49.05) thus obtained, 2.5 c.c. of $H_2SO_4 \cdot 3H_2O$ was added, and the mixture was heated at 140–145°C. for 15 hours. The reaction product obtained was 43.4 g. It was fractionally distilled under reduced pressure and separated into the 1.5 g. unchanged alcohol (b.p. 82–95°C.^{5mm}) and 32 g. hydrocarbons (b.p. 48–82°C.^{5mm}). The hydrocarbons were again fractionally distilled under the normal pressure over metallic sodium 8 times repeatedly.

No.	B.P. °C.	yield %	d_4^{25}	n_D^{25}	$[\alpha]_D$	M.R.		
						obs.	calc. $C_{12}H_{20}$	Δ
1	177–182	1	0.8510	1.4681	+14.17	53.51	52.75	0.76
2	182–185	5	0.8557	1.4702	+15.45	53.49	,,	0.74
3	185–186	11	0.8570	1.4715	+17.51	53.53	,,	0.78
4	186–187	17	0.8567	1.4721	+15.51	53.61	,,	0.86
5	187–188	24	0.8557	1.4731	+15.03	53.77	,,	1.02
6	188–190	6	0.8553	1.4744	+14.01	53.93	,,	1.18
7	190–191	8	0.8543	1.4760	+12.74	54.16	,,	1.41

(43) Balbiano and Paolini, *Ber.*, **35** (1902), 2994; **36** (1903), 3575; **48** (1915), 394.
(44) Tetsusaku Ikeda, *Proc. Sci. Inst. Japan*, **7** (1928), 269; Yasuzi Fujita, *ibid.*, **7**, 1.

No.	Sample B.p. °C.	Wt. g.	Volatile neutral substance
1	177–187	29	21
2	188–191	35	25

Hydrocarbons were put to ozone oxidation in a chloroform solution.

The volatile neutral substances were separated from each other by fractional distillation.

No.	B. p. °C.	yield g.	d_4^{25}	n_D^{25}	Remarks
1	55– 87 7mm	3.3	0.9320	1.4690	colourless
	87– 96	1.8	0.9614	1.4710	faint yellowish green
	96–120	9.0	0.9951	1.4736	faint yellowish green, viscous
2	48– 86	7.0	0.9026	1.4699	colourless
	86– 96	0.5	—	1.4714	faint yellowish green
	96–130	10.6	0.9881	1.4723	faint yellowish green, viscous

Fractions of similar properties were collected together and the mixture was fractionally distilled three times more.

Fraction	B. p. °C.	yield g.	d_4^{25}	n_D^{25}	M. R. obs.	M. R. calc.	Appearance	Analyses obs. C %	Analyses obs. H %
1	51 – 56 7mm	2.0	0.8803	1.4677	51.75	$C_{12}H_{20}F_1$ 52.75	colourless	84.77	11.67
2	56– 74	0.9	—	—	—	—	,,	—	—
3	74– 79	4.5	0.9290	1.4706	49.90	$C_{11}H_{18}O$ 48.61	,,	82.25	11.11
4	79– 90	3.3	0.9525	1.4727	48.85		,,	78.18	11.51
5	90–120	2.9	0.9772	1.4756			yellowish green	75.67	10.24
6	120–126	9.2	1.0124	1.4749	54.52	$C_{12}H_{20}O_2$ 55.41	,,	73.65	10.31
7	126–129	1.6	1.0124	1.4740	54.18		,,	71.55	10.66

Calc. for $C_{12}H_{20}$: C, 87.80; H, 12.20%.
$C_{11}H_{18}O$: C, 79.52; H, 10.84%.
$C_{12}H_{20}O_2$: C, 73.47; H, 10.21%.

Each of the fractions 5–7 decomposed by every distillation and an abundant quantity of acid remained every time. About these acids, some references will be made later. It is considered that fraction 1 is mainly composed of hydrocarbons, fraction 3 contains about 60% of the compound $C_{11}H_{18}O$, fraction 4 is mainly composed of the compound $C_{11}H_{18}O$, fraction 5 contains about 50% of the compound $C_{12}H_{20}O_2$ and the fraction 6 and 7 are both mainly composed of the compound $C_{12}H_{20}O_2$. $C_{12}H_{20}O_2$.

Fractions 3 and 4 were mixed together, and the mixture was fraction-

ally distilled repeatedly to separate out a principal component as follows:

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{10}$	M. R. obs.	M. R. Calc. for $C_{11}H_{18}O$
72–73°C./6 mm	0.9473	1.4712	+27.06	48.87	48.61

(C=2.62 in alcohol)

Found: C, 79.94; H, 11.26. Calculated for $C_{11}H_{18}O$; C, 79.52; H; 10.84%.

Semicarbazone is formed with a great difficulty and it decomposes at 243.6–243.9°C. 2. g. of the oxygen compound described above was reduced with metallic sodium and alcohol, and a reaction product having the following properties was obtained.

B.g.	d_4^{25}	n_D^{25}	$[\alpha]_D^{25}$	M. R. obs.	M. R. Calc. for $C_{11}H_{20}O$
82–86°C/6 mm	0.9581	1.4831	+1.5	50.07	50.12

(C=1.373 in alcohol)

Found: C, 78.25; H, 12.05. Calculated for $C_{11}H_{20}O$; 78.57; H, 11.90%.

The phenylurethane of this substance is a white needle which melts at 147.6–148.7°C.

Fraction 6 was purified by carefully distilling it, and a yellowish green viscous liquid was obtained.

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{10}$	M.R. obs.	M.R. Calc. for $C_{12}H_{20}O_2$	Δ
120–123°C/6 mm	1.0087	1.4746	−6.87	54.60	55.44	−0.84

(C=1.455 in alcohol)

Found: C, 73.39; H, 10.41. Calculated for $C_{12}H_{20}O_2$: C, 73.47; H, 10.21%.

Moreover, the hydrocarbons described above was put to ozone oxidation in its solution in benzene, and the oxidation product thus obtained was distilled under reduced pressure. There was obtained a yellowish green and viscous compound $C_{12}H_{20}O_2$, whose rotatory power was of opposite sign as follows:

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D$	M.R. obs.	M.R. Calc. for $C_{12}H_{20}O_2$	Δ
112–114°C./4 mm	1.0166	1.4749	+38.91	54.27	55.44	−1.17

To 2 g. of the compound $C_{12}H_{20}O_2$, 20 c.c. of nitric acid of 1.29 specific gravity was added. The mixture was heated for 15 hours over a hot water bath and 0.8 g. of an acidic substance was obtained. When it was left alone for a long time, crystals of camphoric acid (m.p. 183°C.) was obtained; and after an analysis made on its silver salt, the following results were obtained: Found: Ag, 52.84. Calculated for $C_{10}H_{14}O_4Ag_2$: Ag, 52.15%.

A reaction product was obtained by reducing 10 g. of the compound $C_{12}H_{20}O_2$ with metallic sodium and alcohol. The reaction product was

separated by steam distillation into a 3.7 g. volatile substance and a 3.4 g. unvolatile substance; and, by fractionally distilling the former, there was obtained a principal component of the following properties:

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{15}$	M.R. obs.	M.R. Calc. for $C_{12}H_{24}O_2$	appearance
140—143°C./6 mm	0.9907	1.4833	−13.31 (C=1.578 in alcohol)	57.71	58.47	faint yellow, viscous

Found: C, 72.18; H, 11.58. Calculated for $C_{12}H_{24}O_2$: C, 72.00; H, 12.00%.

As crystals precipitated out from the latter, they were recrystallised from ether and petroleum ether, and two different compounds were obtained. One of them, a colourless needle crystal (m.p. 82–83°C.), was insoluble in petroleum ether but soluble in both ether and alcohol. The other, a colourless needle (m.p. 114–115°C.) assembled in an asterisk form, was insoluble in petroleum ether and less soluble in ether than the former crystal. Crystal (I) (m.p. 82–83°C.). Found: C, 66.38; H, 11.62. Crystal (II) (m.p. 114–115°C.) C, 65.82; H, 11.63. Calculated for $C_{12}H_{24}O_2 \cdot H_2O$: C, 66.06; H, 11.93%.

These two kinds of crystals were dried at 80°C. under a reduced pressure and put anew to elementary analysis.

	Decrement of wt. by drying	Theoretical number	M.P. after drying
Crystal I (M.P. 82—83°C.)	7.95%	8.26%	83—84°C.
Crystal II (M.P. 114—115°C.)	8.41%	,,	115,8—116.8°C

Crystal (I) Found: C, 71.95; H, 11.99. Crystal (II) C, 71.63; H, 12.41. Calc. for $C_{12}H_{24}O_2$ C, 72.00; H, 12.00%.

To the hydrocarbons (b.p. 185–190.5°C., d_4^{25} 0.8562, n_D^{25} 1.4726, $[\alpha]_D^{11}$ +12.66) described above, some 50% sulphuric acid and glacial acetic acid were added and the mixture was heated at 70–80°C. for 25 hours. A great majority was recovered as unreacted hydrocarbons, and, in addition to these, a small quantity of a polymerisation product was obtained as follows:

B.p.	n_D^{25}	$[\alpha]_D^{21}$	M. R. obs.	M. R. Calc. for $C_{12}H_{20}$	M. R. obs.	M. R. Calc. for $C_{24}H_{38}$
161—162°C/5 mm	1.4966	+14.83	106.6	105.5	106.1	103.3

Found: C, 87.95; H, 12.56. Calc. for $(C_{12}H_{20})_2$: C, 87.80; H, 12.20. Calc. for $C_{24}H_{38}$ C, 88.34; H, 11.66%.

The determination of molecular weight (by Rast's method)

obs.	$(C_{12}H_{20})_2$	$C_{24}H_{38}$
329.5	328	326

(2) *The dehydration of dimethylborneol with phosphorus pentoxide.* 10 g. dimethylborneol was taken drop by drop into a flask, which had

already contained 13 g. phosphorus pentoxide and 30 c.c. petroleum ether. When the generation of hydrogen chloride ceased, the content was left alone for several hours. Then it was thrown into ice water and the reaction product was extracted by the aid of ether. The ether was distilled off and the reaction product was fractionally distilled for several times, and there was obtained the following hydrocarbon.

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{25}$	M. R. obs.	M. R. Calc. for $C_{12}H_{20}F_1$
192—193°C./2 mm	0.8754	1.4765	−5.76	52.38	52.75

Found: C, 87.66; H, 12.13. Calculated for $C_{12}H_{20}$; C, 87.80; H, 12.20%.

When this hydrocarbon was put to ozone oxidation, a single oxidation compound $C_{12}H_{20}O_2$ was obtained as follows:

B.p.	d_4^{25}	n_4^{25}	$[\alpha]_D^{25}$	M. R. obs.	M. R. Calc. for $C_{12}H_{20}O_2$
100—105°C./2 mm	1.0026	1.4765	−17.78	55.20	55.44

Found: C, 73.34; H, 10.49. Calculated for $C_{12}H_{20}O_2$: C, 73.47; H, 10.21%.

This compound, to be considered as a diketone, has decomposed during distillation, forming an acidic substance, which gave trans-camphoric acid (m.p. 174°C.) when recrystallised by the aid of ether and petroleum ether. Found: C, 29.29 H, 3.39 Ag, 52.96. Calculated for $C_{10}H_{14}O_4Ag_2$: C, 29.00; H, 3.38; Ag, 52.15%.

(3) *The dehydration of dimethylborneol with phthalic anhydride.* Dimethylborneol was dehydrated, heating it with phthalic anhydride, and the following hydrocarbon was obtained.

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{18}$	M. R. obs.	M. R. Calc. for $C_{10}H_{20}F_1$
179—196°C./3 mm	0.8556	1.4710	+7.13	53.44	52.75

Found: C, 87.69; H, 12.50. Calculated for $C_{12}H_{20}$: C, 87.80; H, 12.20%.

To our regret, the quantity of the sample being very small, we could not continue the research further.

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